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Asphaltene stability in crude oil during carbon dioxide injection and its impact on oil recovery: A review, data analysis, and experimental study

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ASPHALTENE STABILITY IN CRUDE OIL DURING CARBON DIOXIDE INJECTION AND ITS IMPACT ON OIL RECOVERY: A REVIEW, DATA ANALYSIS, AND EXPERIMENTAL STUDY

by

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ABSTRACT

Crude oils are usually associated with many compounds, some of which are favorable and others, which are not. One of the most unfavorable components of crude oil that pose severe operational problems and decreases oil production significantly are asphaltenes. These compounds are solids that are homogenized in the crude oil at room temperature but tend to separate from solution when agitated. They can deposit in the reservoir pores, wellbore, and transportation pipelines thus causing severe operational problems and oil recovery reduction.

Even though researchers have been studying asphaltenes for more than 100 years, there is still an ambiguity concerning asphaltene structure and characteristics since asphaltenes have no unique structure. This research performed a comprehensive data analysis on both laboratory studies and field cases involving asphaltene in order to provide a generalized guideline on asphaltene properties asphaltene stability. The analysis was based on more than 200 references involving more than 4000 experiments and 19 field studies. Two statistical analysis tools were used, including histograms and boxplots.

After determining the factor impacting asphaltene, this research conducted experiments to understand the impact of these factors on asphaltene stability in crude oil during carbon dioxide (CO_2) injection in unconventional shale nanopores, since very limited research has been conducted in this area. The research investigated the impact of several factors including pressure, temperature, oil viscosity, pore size, porous media thickness, and heterogeneity on asphaltene precipitation, pore plugging, and oil recovery reduction. A Pareto Plot was also generated to determine the factor that had the strongest impact on asphaltene instability in the crude oil.

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TABLE OF CONTENTS

Page

PAPER

LIST OF ILLUSTRATIONS

LIST OF TABLES

1. INTRODUCTION

1.1. STATEMENT AND SIGNIFICANCE OF THE PROBLEM

When producing crude oil from reservoirs, the oil is usually associated with many components. One of the components of the crude oil that usually causes many severe problems during operations is asphaltene (Fang, T. et al., 2018). Asphaltenes are extremely complex in structure and vary, sometimes significantly, from one another in properties, composition, and molecular shape which makes them overwhelming components of crude oil to analyze and study, even after more than 100 years of investigating them (Monger, T.G. and Fu, J.C., 1987).

Since they have no unique structure, asphaltenes are usually classified as a solubility class (Pan, H. and Firoozabad, A., 1997). This makes them difficult to study since each structure has to be investigated and analyzed separately. Adding to this complexity, it has been found that many factors will impact asphaltene stability in the crude oil, and since asphaltenes vary in properties based on their structure, they will be impacted differently (Ocanto, O. et al., 2009). It is therefore imperative that a comprehensive understanding of all the different asphaltenes and the factors impacting them be provided; alas, no comprehensive data analysis has yet been conducted to cover all reported cases of asphaltene and factors impacting them.

Asphaltenes are one of very few components in crude oils that are solids (Schantz, S. and Stephenson, W., 1991). At equilibrium conditions, they are homogenized in the crude oil, however, should this equilibrium be disturbed, the asphaltene becomes prone to precipitating from solution and may even begin to deposit in the reservoir, wellbore, and even transportation pipelines (Speight, J.G. and Moschopedis, E., 1981). This can result in several operational, production, and transportation problems, which are sometimes extremely difficult and costly to mitigate. Asphaltene severity in pore plugging will increase furthermore in smaller pores, usually associated with unconventional reservoirs (Shen, Z. and Sheng, J., 2008). This can result in the cessation of oil production altogether, and is extremely difficult to mitigate as well. Asphaltene pore plugging has not been extensively researched in unconventional reservoirs, and could prove to be one of the main reasons behind the failure of enhanced oil recovery (EOR) application in some shale reservoirs across the United States (Fakher, S. and Imqam, A., 2018a).

Based on the aforementioned, asphaltenes are extremely complex in structure and composition, and no research has performed a comprehensive analysis of all asphaltene properties and factors impacting them. Also, asphaltene pore plugging has not been extensively researched in unconventional reservoirs due to the novelty of the application of EOR in shale reservoirs. Further investigation is therefore required to both comprehensively determine the properties of asphaltenes and the factors impacting them, along with their impact on asphaltene pore plugging in nanopores of unconventional shale reservoirs.

1.2. EXPECTED IMPACTS AND CONTRIBUTION

The findings obtained from this research can help clarify part of the ambiguity related to asphaltenes in the oil industry by providing a comprehensive analysis of all published results pertaining to asphaltene in crude oil. The research will also help shed light on the impact of asphaltene on oil recovery and pore plugging in unconventional shale reservoirs, which is considered an extremely novel topic that very few researchers have investigated. Based on this, the expected impacts of this research and its contribution on advancing the knowledge pertaining to asphaltenes in the hydrocarbon industry can be summarized as follows:

- Provide a comprehensive data analysis on the properties of asphaltene and the main factors that impact it.
- Illustrate the most frequently observed ranges for different parameters affecting asphaltene in both laboratory studies and field cases.
- Present a guideline on the expected impact of different parameters under all reported conditions on asphaltene stability in crude oil.
- Show the factors that have the strongest impact on asphaltene stability in crude oil during CO_2 injection.
- Convey the severity of asphaltene pore plugging in unconventional shale reservoirs and its impact on oil recovery.

1.3. OBJECTIVES

The overall objective of this research is to provide a comprehensive guideline to the properties of asphaltenes and the factors that will impact asphaltene stability in the crude oil during CO_2 injection and then quantify the impact of these factors on oil recovery and pore plugging in unconventional shale reservoirs with nanopores. In order to reach this objective, the research was divided into several tasks, each with their own unique objective. These objectives are summarized as follows:

- To provide a comprehensive literature review on the main characteristics of asphaltenes in crude oil and illustrate the currently available methods to study the asphaltene properties and structure.
- Determine asphaltene phases in the crude oil and how to overcome the formation of asphaltene deposits in the reservoir, wellbore, and pipelines.
- Perform a comprehensive data analysis based on laboratory experiments and field studies involving asphaltene in crude oil the determine to factors that have the strongest impact on asphaltene stability in crude oil and characteristics of asphaltene in different crude oils from around the world.
- Compare the laboratory and field results obtained from the data analysis to illustrate the difference in ranges between the lab and field studies.
- Perform experiments based on the factors determined in the data analysis task to understand the impact of asphaltene on pore plugging and oil recovery in unconventional nanopores during CO_2 injection.
- Study asphaltene stability in crude oil during CO_2 injection and the factors impacting asphaltene precipitation during CO_2 injection in nanopores.

1.4. SCOPE OF WORK

In order to meet the mentioned objectives, this research was divided into three main tasks. These tasks are presented in Figure 1.1 below. The first task involves performing a comprehensive literature review on asphaltene properties and characteristics in order to understand what previous researchers have done to study asphaltene, and to determine asphaltene behavior in crude oil under different conditions. The literature review also helped determine the asphaltene phases, and the factors that have the strongest impact on asphaltene stability in crude oil and how to overcome asphaltene related problems in the field. The second task involves undergoing a comprehensive data analysis on all reported laboratory and field work involving asphaltene in order to provide a comprehensive understanding of asphaltene characteristics from crude oils worldwide, and to determine the factors that have the strongest impact on asphaltene stability in the crude oil and the ranges at which these impacts were reported in the literature. The final task is to perform an extensive experimental study on the factors that were determined from the data analysis task to have the strongest impact on asphaltene stability during CO_2 injection. This task focuses on asphaltene impact on reducing oil recovery in nanopores through pore plugging at different conditions and using different viscosity oils. By undergoing these three tasks, a more detailed understanding of asphaltene can be provided to the industry in hopes that asphaltene damage can be reduced in both laboratory experiments and field cases that involve both conventional and unconventional reservoirs.

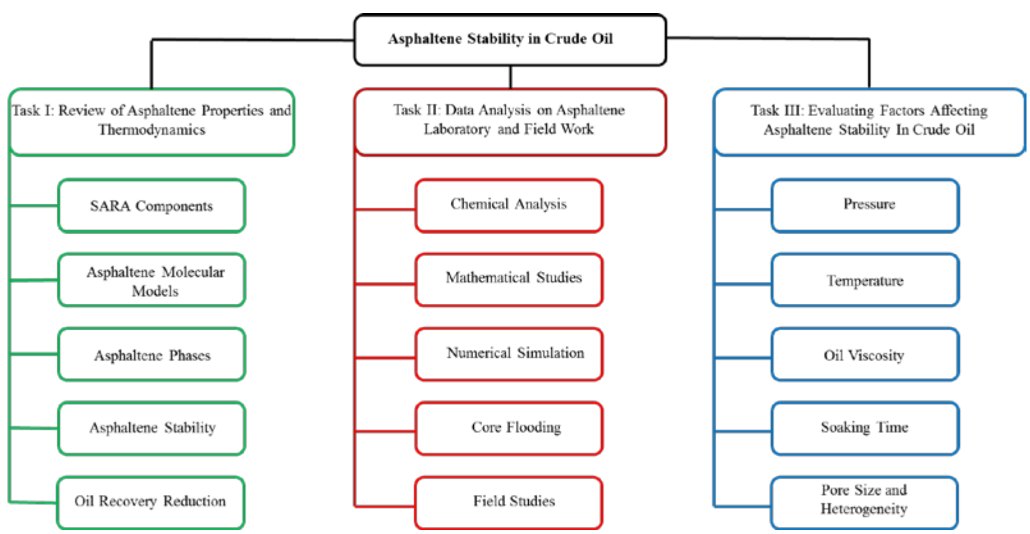

Figure 1.1. Asphaltene Research Scope of Work

2. LITERATURE REVIEW

2.1. CRUDE OIL COMPONENTS

Crude oil components can be divided into multiple compounds and subdivisions based on the composition of the crude oil. Normally, crude oil will contain a percentage of dissolved gasses, liquids, and solids. The liquids can be further divided into saturates, aromatics, and resins. Different types of solids may also exist in the crude oil, however, the most prominent is asphaltene (Ashoori, S. et al., 2006; 2017). These components are usually grouped together as Saturates-Aromatics-Resins-Asphaltenes, more commonly referred to as SARA analysis. The SARA analysis is performed using chromatography to determine the presence, and concentration of these components. The exact description of each of these components and their relation to the asphaltene is explained below (bisht, H. et al., 2013).

2.1.1. Saturates. Saturates are the nonpolar compounds in the hydrocarbon that are saturated, and thus do not contain any double bonds. These compounds are not soluble in water, as are most of the components of the crude oil. The carbon atoms are bonded to the maximum allowable hydrogens, and thus no carbon-carbon double bonds are present. They are the most commonly known hydrocarbons since they play a strong role in the overall structure of the crude oil (Goel, P. et al., 2017). Saturated hydrocarbons are generally referred to as alkanes. Alkanes have a general structure that is represented as C_nH_{2n-2}, which means that for each carbon atom there are two plus two hydrogen atoms in the alkane molecule. The simplest alkane compound is methane, followed by ethane and propane. The structure of all three is shown in Figure 2.1 below. As can be seen, no double bonds are present in the compound. Saturates are one of the main liquid, or gas in regards to methane, components of the hydrocarbon; asphaltenes are in solution within these compounds until it becomes unstable and asphaltenes begin to precipitate from solution (Angle, C.W. et al., 2015).

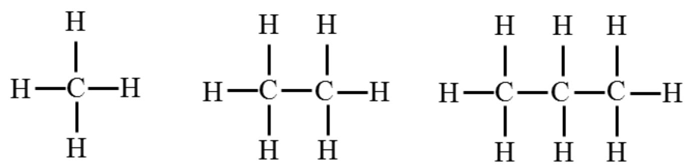

Figure 2.1. Molecular Structure of Methane, Ethane, and Propane

2.1.2. Aromatics. Aromatics are the second main component of hydrocarbons. These compounds are slightly more complex in structure than saturates. They are nonpolar, and are characterized by an unsaturated hydrocarbon ring, with multiple carbon-carbon double bonds within the ring configuration (Keshmirizadeh, E.S. et al., 2013). Figure 2.2 shows the structure of three common aromatics, including toluene, xylene, and phenolic acid. All three of these compounds has a cyclic hydrocarbon ring attached to a functional group.

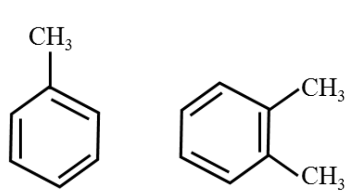

Figure 2.2. Molecular Structure of Toluene, Xylene, and Phenolic Acid

2.1.3. Resins. Resins are considered much more complex in structure compared to saturates and aromatics. They are higher in molecular weight compared to the two previous components as well. Resins play a significant role in the stabilization of the asphaltene in the crude oil (Leon, O. et al., 2002). The crude oil in general is nonpolar, which means it is insoluble in water (Lammoglia, T. and Filho, C.R., 2011). Asphaltenes are highly polar in nature and thus cannot be homogenized or solubilized in the crude oil by their own since it is against their nature. Resins are characterized by having both a polar and a nonpolar side and thus function as a bridging material that connects the nonpolar hydrocarbon compounds to the highly polar asphaltene (Miadonye, A., and Evans, L., 2010). Figure 2.3 shows a typical structure of a resin molecule.

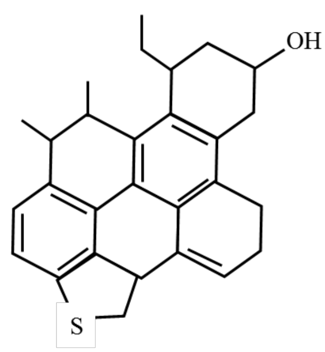

Figure 2.3. Molecular Structure of Simple Resin Molecule

2.1.4. Asphaltenes. Asphaltenes are considered one of the most complex components of crude oils. They are one of the very few components that are solid, shown in Figure 2.4. Asphaltene complexity comes mainly in the way their structure is defined. All of the three previously explained components have a general structure by which they can be classified. Unfortunately, asphaltenes have tens of different structures, which makes generalizing them into a specific family very difficult (Pazuki, G.R., 2007). Asphaltenes are generally classified as a solubility class since they are characterized as being insoluble in n-alkanes. There are several characteristics that can be used to identify asphaltenes including (Seifried, C. et al., 2013):

- **Solid:** Asphaltenes are a solid phase that is homogenized in the crude oil at reservoir conditions.
- **n-Alkane Insoluble:** Asphaltenes are classified as a solubility class since they have several structure and thus it is extremely difficult to provide a generalized structure for them. They are therefore defined as the highest molecular weight components in the crude oil that are insoluble in light n-alkanes such as n-pentane or n-heptane and soluble in aromatics such as toluene or xylene.
- **Highly Polar:** Asphaltenes are one of very few components of crude oil that are highly polar, in contrast to the crude oil as a whole, which is considered nonpolar.
- **Heteroatoms:** Asphaltenes are associated with heteroatoms, mainly manifested in nitrogen, oxygen, and sulfur.

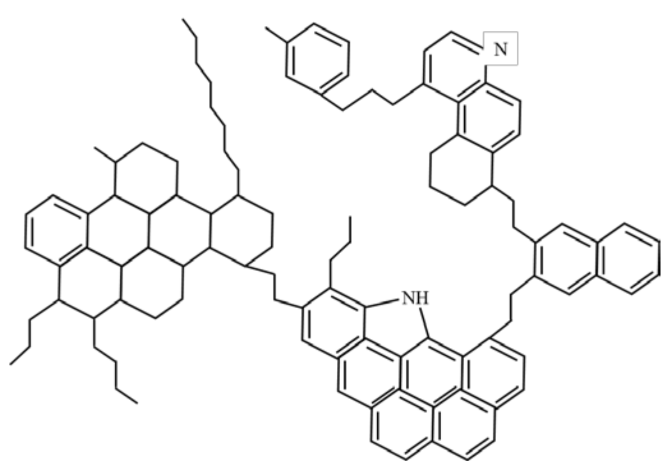

Figure 2.4. Molecular Structure of an Asphaltene

2.2. SARA ANALYSIS

The analysis of the four components including Saturates, Aromatics, Resins, and Asphaltenes, is referred to as the SARA analysis. The main aim of the SARA analysis is to differentiate between, and quantify the four main components of the crude oil (Bissada, K.A. et al., 2016). Figure 2.5 provides a flowchart of the SARA analysis steps to differentiate between the different components of the crude oil. If a sample of crude oil is added to liquid propane, the aromatics and saturates will be solubilized, whereas the resins and asphaltenes will precipitate. This will help isolate the resins and the asphaltenes. Several methods can be applied to differentiate between the aromatics and saturates, including gas chromatography. The resin and asphaltene precipitate can then be taken and dissolved in a light n-alkane, most notably n-pentane and n-heptane. The resin will be soluble in the n-alkane whereas the asphaltene will not, and will precipitate. Using this procedure, the asphaltene can be distinguished from the resin. Using this method, all four components of the SARA analysis can be accurately differentiated.

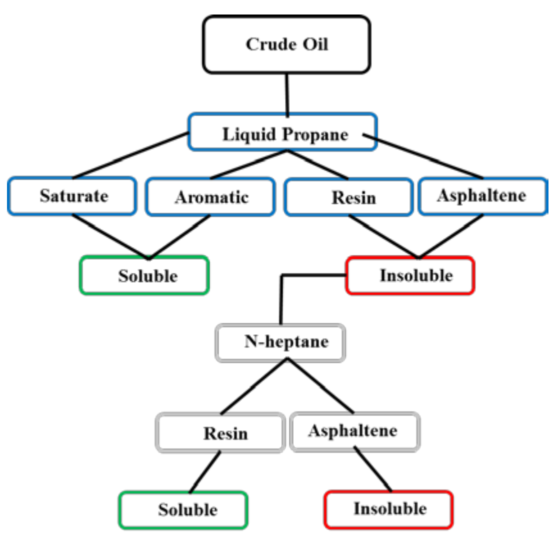

Figure 2.5. SARA Analysis Flowchart

2.3. ASPHALTENE STRUCTURE AND COMPOSITION

Asphaltenes are extremely complex in nature. Also, they are usually classified as a solubility class rather than a specific structure due to the several varieties of structures available for asphaltenes. Several models have arisen in attempt to provide a standard method that would be able to encompass all the different asphaltene chemical structures and model them (Bahman, J. et al., 2017).

2.3.1. Archipelago. The archipelago asphaltene model, in accordance with its name, models the asphaltene structure as several aromatic rings connected together through aliphatic chains. An example of the Archipelago model is shown in Figure 2.6 below. Several aromatic rings appear as separate groups connected together using several aliphatic chains. There is an uncertainty in the model regarding the number of aromatic rings present in the asphaltene molecule however. The side chains are believed to have an average length of 5-7 carbons.

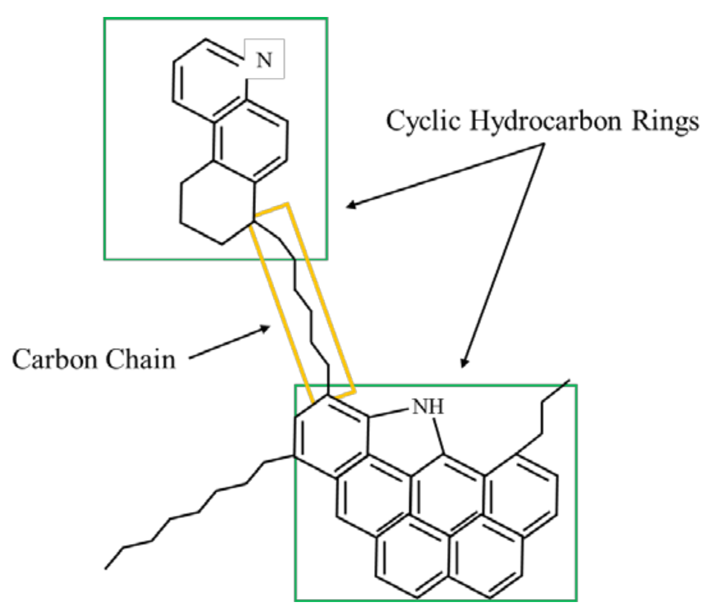

Figure 2.6. Archipelago Asphaltene Structure Example

2.3.2. Continental. The continental model proposed the structure of asphaltene as a large group of aromatic rings in the middle of the asphaltene molecule connected to several aliphatic branches. This model is usually associated with lower molecular weight asphaltenes, and is hence referred to as the condensed aromatic model.

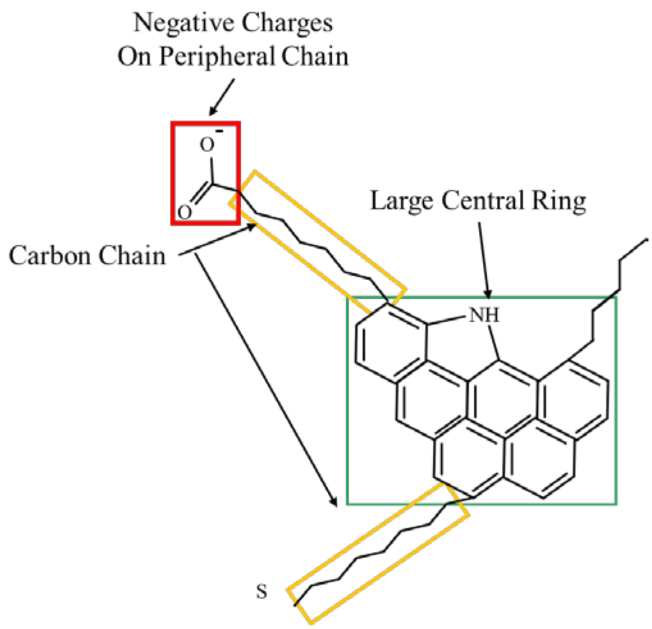

Figure 2.7. Continental and Anionic Continental Structure

2.3.3. Anionic Continental. The Anionic Continental is extremely similar in structure compared the Continental model, shown in Figure 2.7. The major difference lies in a negatively charged group attached to one of the aliphatic chains attached to the main structure. This gains the asphaltene structure a negative charge, which adds to the change in potential of the asphaltene which will impact asphaltene stability significantly; this is referred to as the electrokinetic effect and will be explained in details later on.

2.3.4. Yen-Mullins. The Yen-Mullins model is the most widely accepted asphaltene model nowadays, shown in Figure 2.8 (Mullins, O.C., 2011). This model describes that asphaltene structure based on size and behavior as a function of the crude oil that bears the asphaltene. In light oils, with high API gravity, the asphaltenes will be present as small poly-aromatic hydrocarbon molecules with an average diameter of 1.5 nanometer. In this case, the asphaltene concentration will be relatively low, and thus the asphaltene size will not grow. In black oils, with slightly less API gravity, the asphaltene concentration will be higher, and thus the asphaltene will be present in the form of nanoaggregates with an average diameter of 2 nanometer, which is slightly larger than the asphaltene present in the light oil. In heavy oils, with extremely low API gravity, the asphaltene concentration will be relatively high, and will thus begin to form clusters. These cluster will grow in size, and will reach an average diameter of 5 nanometers. The clusters form from the combination of several nanoaggregates together. Based on this model, as the asphaltene concentration in the oil increases, the oil will become heavier, due to the high molecular weight of asphaltenes, and thus its API will decrease, which shows that asphaltenes have an overall negative impact.

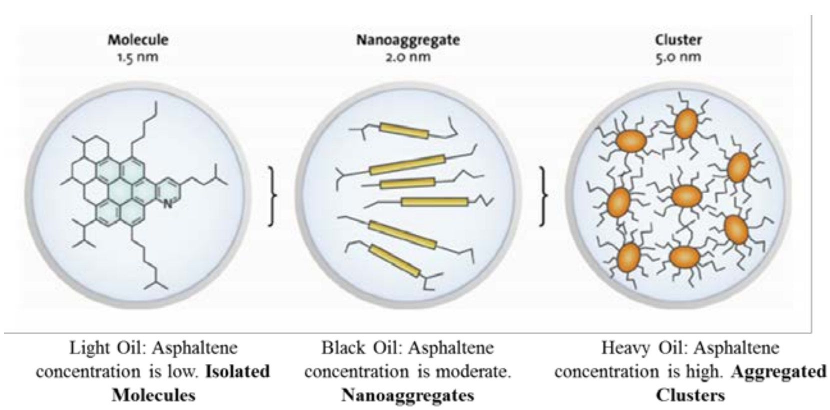

Figure 2.8. Yen-Mullins Asphaltene Model (Mullins, O.C., 2011)

2.4. ASPHALTENE STABILITY IN CRUDE OIL

Asphaltenes are highly polar compounds whereas the crude oil is nonpolar in nature. It is therefore impossible for the asphaltene to be homogenized in the crude oil on its own. Asphaltenes are stabilized in the crude oil via resins that have both a polar and a nonpolar side to their structure and thus act as a bridging material that connects both the asphaltene and the other nonpolar components of the crude oil (Nahid, S.M., 2003). There are several attraction forces that act on the crude oil to homogenize its many components. These forces include Coulomb forces, Electronegativity, Polarity, and Polarization. These forces are illustrated in Figure 2.9.

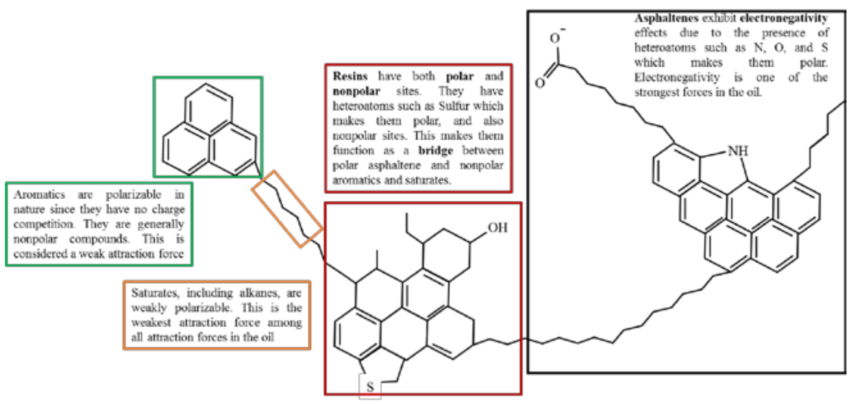

Figure 2.9. Crude Oil Interaction Forces

2.5. ASPHALTENE DETECTION AND CHEMICAL ANALYSIS

Since asphaltenes are extremely complex in structure and vary in composition and size, several methods are used to detect and study asphaltene structure and composition in the crude oil. These methods function to determine several aspects of the crude oil and vary in terms of how they detect the asphaltenes and their accuracy. Some of these methods can even perform the SARA analysis by determining the different fractions of the crude oil and their compositions. Table 2.1 summarizes most of the methods used to study asphaltenes based on different studies found along the years.

Table 2.1. Summary of Chemical Analysis Methods of Asphaltene Along the Years

Reference	Year	Analysis Technique
Jewell, D.M. et al.	1972	Anion-Cation Exchange Chromatography
Lichaa, P.M. and Herrera, L.	1975	Asphaltene Precipitation Tests
Hernandez, M.E. et al.	1983	SARA Analysis
Pearson, C.D. and Gharfeh, S.G.	1986	Liquid Chromatography with Flame Ionization Detector
Karlsen, D.A. and Larter, S.R.	1991	Thin Layer Chromatography with Flame Ionization Detector
Martinez, M.T. et al.	1997	Thermal Cracking
Kok, M.V. et al.	1998	Oxidation Reaction and SARA Analysis
Groenzin, H. and Mullins, O.C.	2000	Fluorescence Depolarization
Yarranton, H.W. et al.	2000	Vapor Pressure Osmometry
Fan, T. et al.	2002	Clay-Gel Adsorption Chromatography, Thin-Layer Chromatography, and High Pressure Liquid Chromatography
Islas-Flores, C.A. et al.	2005	Open Column Chromatography and High Pressure Liquid Chromatography SARA Analysis
Hannisdal, A. et al.	2006	Infrared Analysis
Abudu, A. and Goual, L.	2009	Adsorption using Microbalance
Miadonye, A. and Evans, L.	2010	Calorimetry and Filtration
Bahzad, D. et al.	2010	Hydrodematallization
Angle, C.W. and Hua, Y.	2011	Dynamic Light Scattering Microscopy
Cho, Y. et al.	2012	Fourier Transform Ion Cyclotron Resonance Mass Spectrometry with Atmospheric Pressure Photoionization
Keshmirizadeh, E. et al.	2013	Open Column, Thin Layer, and Gas Chromatography Coupled with Flame Ionization Detector
Kharrat, A.M. et al.	2013	Optical Spectroscopy Method
Seifried, C.M. et al.	2013	Confocal Laser-Scanning Microscope
Cendejas, G. et al.	2013	Nuclear Magnetic Resonance
Fakher, S. et al.	2018	SARA Analysis using Chemical Methods based on Heptane Separation
Fakher, S. and Imqam, A.	2018	Filtration based on Heptane
Fakher, S. and Imqam, A.	2018	SARA Analysis and Gas Chromatography

2.6. ASPHALTENE PHASES IN CRUDE OIL

The asphaltene will pass by several phases in the crude oil based on its stability and how well it remains in solution under the thermodynamic and operational conditions at which the oil is being produced (Nghiem, L.X. and Coombe, D.A., 1997). The different phases that the asphaltene can pass by are shown in Figure 2.10 Each of these phases will be explained in details.

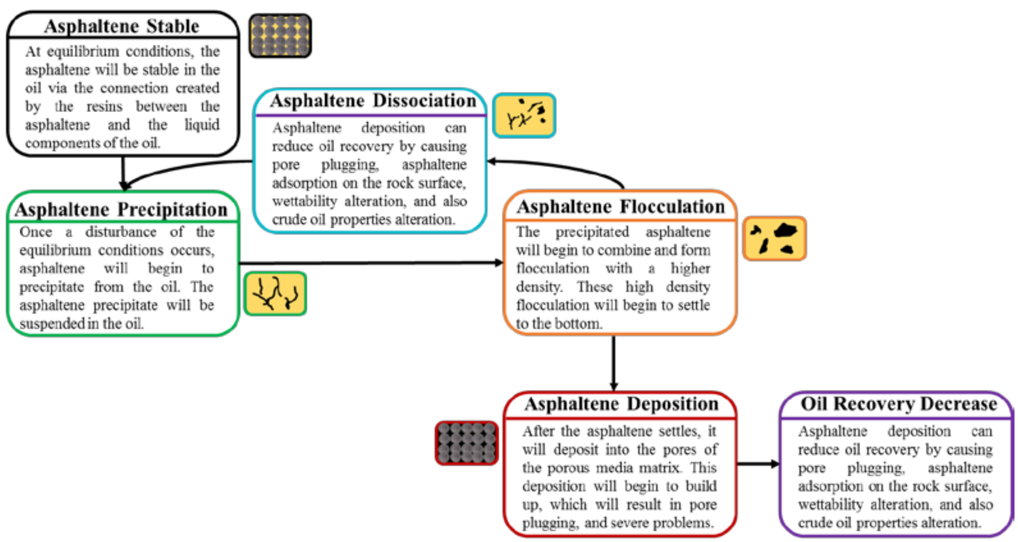

Figure 2.10. Asphaltene Phases in Crude Oil

2.6.1. Asphaltene Precipitation. At equilibrium conditions, the asphaltene will remain stable in the crude oil. Once any disturbance, such as production or solvent injection, occurs to the oil however, the asphaltene will begin to precipitate from the oil solution. Precipitation involves the asphaltene solid coming out of solution and forming visible asphaltene particles that are suspended in the oil. Since the asphaltene is still suspended in the oil, it still does not pose a large threat. The asphaltene will still be mobile with the oil, as long as the precipitation does not continue to increase further.

2.6.2. Asphaltene Flocculation. If asphaltene precipitation increases, the asphaltene particles will begin to combine and form larger asphaltene flocculations with a higher density than the previously precipitated particles. These dense flocculations can pose a serious threat since the particles have a large density and thus will begin to deposit in the reservoir pores, wellbore, or pipeline.

2.6.3. Asphaltene Dissociation. If the flocculated asphaltene particles are noticed early, they can be remediated relatively easily. If a proper remedial method is applied, the flocculations can be broken down and dissociated back into the smaller precipitated particles. If this occurs, the precipitated particles can then be homogenized in the crude oil again, usually using a stabilizing chemical reagent.

2.6.4. Asphaltene Deposition. If the asphaltene flocculations are not immediately noticed and are left in the oil, these flocculations will begin to deposit. If a large volume of asphaltene is deposited, it will cause severe problems such as pore plugging in the reservoir, wellbore plugging due to asphaltene buildup, or buildup in pipeline, which will incontrovertibly result in catastrophic problems if not detected early.

2.7. FACTORS IMPACTING ASPHALTENE STABILITY

Asphaltene stability in the crude oil can be impacted by many factors (Rogel, E. at al., 1999; 2003). These factors can be grouped into operational factors, which are factors that are applied during production from the reservoir, and reservoir factors, which are factors that are originally native to the reservoir but are affected as production, or fluid injection commences. The chart presented in Figure 2.11 shows the main factors that fall under operational and reservoir factors. These factors will be explained in details in this section.

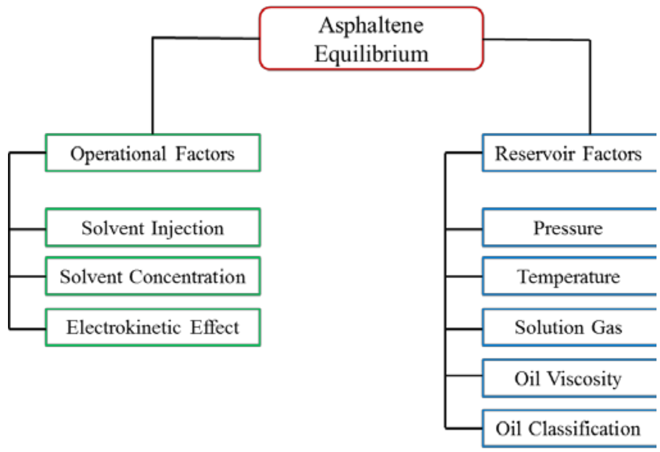

Figure 2.11. Factors Impacting Asphaltene Equilibrium

2.7.1. Reservoir Conditions. The reservoir conditions usually involve the reservoir thermodynamics, including pressure and temperature, and the oil properties, including solution gas, oil viscosity, and the oil classification based on its API gravity. The reservoir pressure and temperature usually do not change, and are thus uncontrollable. Regarding the oil properties, these will change depending on the production mechanism, injected fluids inside the reservoir, and change in pressure as the hydrocarbon is mobilized.

2.7.2. Solvent Injection. A solvent is any material that can be solubilized in the crude oil at different conditions based on the solvent and the reservoir properties. Several solvents can be injected into the reservoir including steam, surfactant, CO_2, nitrogen, methane, and many other solvents that are used to alter the properties of the crude oil. As the solvent begins to interact with the oil, the asphaltene might no longer be stable in the crude oil due to a shift in its initial equilibrium conditions at which it was initially solubilized in the oil.

2.7.3. Electrokinetic Effect. From its structure, the electrokinetic effect refers to the movements of a substance due to a change in charges. Asphaltenes usually carry a charge, and thus during production operations, a drawdown is induced due to the difference in reservoir and wellbore pressure. This drawdown, along with the asphaltene charge, are two of the main reasons behind the electrokinetic effect, which will result in asphaltene instability in the crude oil, and eventually, asphaltene precipitation.

2.8. ASPHALTENE RESERVOIR PROBLEMS DURING PRODUCTION

Once asphaltene deposition occurs, several problems can result in the reservoir. These problems can include pore plugging, adsorption of the asphaltene to the rock grains, and wettability alternation of the rock from its original wettability to oil wet (Soroush, S. et al., 2014). All of these occurrences will have a strong impact on oil recovery, and are considered relatively difficult to mitigate, shown in Figure 2.12.

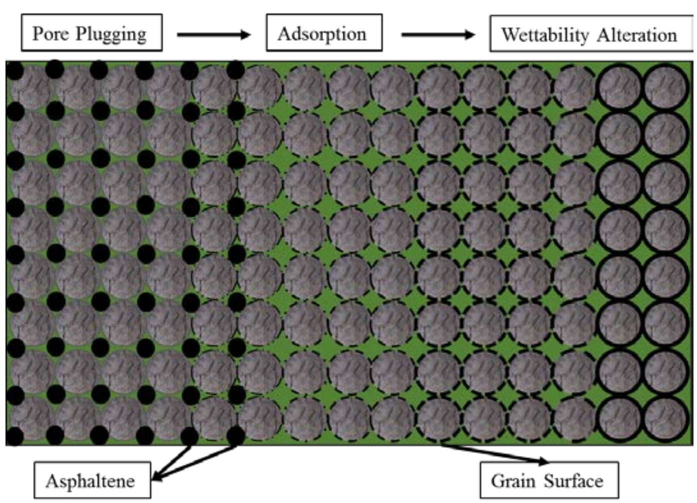

Figure 2.12. Asphaltene Impact on Oil Recovery

2.8.1. Pore Plugging. If the asphaltene begins to deposit in the reservoir pores, this deposition will begin to buildup, and eventually fill up all the available voids in between the pores. This will result in the pores being plugged. This pore plugging will deter, or completely hinder the flow of the oil, and will thus affect the oil recovery significantly in a negative manner.

2.8.2. Adsorption and Wettability Alteration. If the asphaltene deposition increases to a great length, the asphaltene will begin to adsorb onto the grain surface. This adsorption will result in the grains being surrounded by the asphaltene, which is a component of the crude oil, and thus will result in the wettability of the oil to become strongly oil wet. This will decrease the relative permeability of the oil and decrease oil recovery.

2.9. ASPHALTENE SEVERITY IN UNCONVENTIONAL RESERVOIRS

As the aforementioned illustration depicted, asphaltene can cause severe damage to the reservoir and may reduce or completely cease oil production. As the pore size decreases, asphaltene deposition will fill up the voids much faster due to a reduction in the available space. Very few researchers have investigated asphaltene pore plugging in unconventional shale reservoirs due to the relative novelty of the producing from unconventional shale reservoirs compared to conventional shale reservoirs, especially for EOR applications in unconventional shale reservoirs (Shen, Z. and Sheng, J., 2016). It is therefore extremely important to investigate asphaltene pore plugging in unconventional reservoirs since this could be one of the main reasons why EOR applications in some shale plays failed significantly even though it was successful in others.

PAPER

I. ASPHALTENE COMPREHENSIVE DATA ANALYSIS BASED ON LABORATORY AND FIELD RESULTS

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ABSTRACT

Crude oil has multiple components within it that are either favorable for production, or unfavorable due to the severe problems that they pose both during production, and during the processing phase of the oil. Asphaltene is a solid component of crude oil that is usually solubilized in the oil at reservoir conditions, but can separate and deposit in the pores of the reservoir, hence causing severe operational damages and a large reduction in oil recovery. Several experimental researches have been conducted to evaluate asphaltene concentration, particle and aggregate size, elemental content, precipitation, flocculation, deposition, pore plugging, adsorption, and wettability alteration. These experimental works contain more than thirty different analysis techniques and methods. In addition, multiple field tests have been reported on asphaltene damage to reservoirs in several fields worldwide. This research aims to provide a comprehensive and detailed data analysis on asphaltene properties, and the factors affecting asphaltene equilibrium to determine the working conditions at which asphaltene has been studied, and the main properties of asphaltene in crude oil. The data collected included 219 laboratory studies including more than 4000 experiments and 19 field studies from countries across the globe. The data

analysis involved gathering and cleaning of the data, homogenizing the units, and then analyzing the data using two statistical analysis tools including histograms and boxplots. The figures generated using these two statistical analysis tools include asphaltene properties, heteroatoms concentration, crude oil properties, thermodynamic conditions, and core flooding or field properties. To the authors' knowledge, no comprehensive data analysis has been performed on asphaltene in crude oil, which makes this research significant in terms of determining the lab and field properties that mostly affect asphaltene in crude oil and the working condition affecting asphaltene equilibrium.

1. INTRODUCTION

Crude oils are extremely complex in terms of properties and composition. They can contain hundreds of different components with different properties and characteristics. One of the most complex components of crude oil are asphaltenes. Asphaltenes have different structure and sizes based on the crude oil properties, and thus are usually classified based on their solubility in light n-alkanes, such as n-heptane, rather than a specific structure (Boussingault, J.B., 1837). Since asphaltenes are solid, if they precipitate from the crude oil and form dense flocculations, they can begin depositing in the reservoir, wellbore, or even equipment and pipelines.

Due to the complexity of asphaltenes, understanding their concentration in different crude oils, and quantifying the factors impacting asphaltene precipitation and deposition is extremely important in order to avoid the problems associated with asphaltenes in both lab experiments and field operations. Since asphaltenes have tens, or perhaps even hundreds, of different structures, many methods have been used to detect and analyze asphaltenes. One of the most widely used methods is the SARA analysis (Hernandez, M.E. et al., 1983) which can be determined using several techniques such as anion and cation exchange chromatography (Jewll, D.M. et al., 1972), column separation and flame ionization chromatography (Fan, T. et al., 2002), gas chromatography coupled with mass spectrometry (Fakher, S. and Imqam, A., 2018a; Fakher, S. et al., 2018) and liquid chromatography (Hinkle, A. et al., 2008). Other chemical analysis focused on the composition of the asphaltene itself using hydrodematallization (Seki, H. and Kumata, F., 2000), x-ray diffraction, vapor pressure osmometry (Dickie, J.P. and Yen, T.F., 1967), light scattering microscope (Angle, C.W. and Hua, Y., 2011), Fourier transform infrared spectroscopy (Cho, Y. et al., 2012), infrared analysis (Hannisdal, A. et al., 2006) and more recently, computer tomography scanning (Alrashidi, H. et al., 2018), and confocal laser-scanning microscope (Seifried, C.M., et al., 2013). Some research also investigated the molecular structure of the asphaltene using molecular simulation and thermodynamic Micellization modelling to study the behavior of the asphaltene molecule and its characteristics (Mullins, O.C., 2011; Victorov, A.I., and Firoozabadi, A., 1996). These researches indicate that multiple methods are needed in order to accurately understand the characteristics of asphaltenes which shows the extent to which asphaltenes are complex, and emphasizes the need to obtain a comprehensive understanding of asphaltenes in different crude oils with different structures and compositions.

Asphaltene pore plugging is a severe phenomenon that can have a strong impact on oil recovery. Pore plugging has been researched extensively using mainly core flooding experiments (Lichaa, P.M. and Herrera, L., 1975). Several core types have been investigated for asphaltene pore plugging severity, along with different crude oils from several light, intermediate, and heavy oil reservoirs (Wang, S. et al., 2016; Monger, T.G. and Fu, J.C., 1987; Rivastava, R.K. and Huang, S.S., 1997; Yen, A. et al., 2001; Shedid, S.A. and Zekri, A.Y., 2006; Mendoza, J.L. et al., 2009; Behbahabi, T.J. et al., 2012; Kazempour, M. et al., 2013; Soroush, S. et al., 2014; Shen, Z. and Sheng, J., 2018). These researches used multiple core types including carbonates, sandstones, shales, composite cores, sand pack and glass beads to investigate asphaltene pore plugging. Many researchers have also reported field studies where asphaltene caused severe operational problems, and oil production decrease. Mitigation mechanisms have also been reported, mainly manifested in chemical methods, including the injection of a chemical to re-dissolve the asphaltene, and mechanical methods, such as water jetting or drilling through the asphaltene buildup in the wellbore (Thawer, R. et al., 1990; Schantz, S.S. and Stephenson, W.K., 1991; Yen, A. et al., 2001; Iwere, F.O. et al., 2002; Al-Ghazi, A.S. and Lawson, J., 2007; Abdallah, D. et al., 2010; Uetani, T., 2014). These studies demonstrate how asphaltenes can cause severe problems in different reservoirs and formations worldwide, and thus understanding and combing the parameters that these researchers have faced and investigated is paramount in fully understanding how to overcome the asphaltene pore plugging predicament and thus avoid complications during experimental work and field production.

Even though there are many researchers studying asphaltenes, no data analysis has yet been performed on asphaltene properties and the factors impacting asphaltene equilibrium. Since asphaltenes are extremely complex and cause severe problems in many reservoirs worldwide, it is important to provide a guideline to the ranges and values reported for asphaltene concentrations and factors influencing asphaltene precipitation and pore plugging in laboratory experiments and hydrocarbon reservoirs. This research undergoes a comprehensive data analysis on asphaltene in crude oil based on both laboratory and field data using two major statistical analysis tools including histograms and boxplots to increase the ability to better predict asphaltene precipitation and the extent to which it may result in problems based on the rock and fluids condition in both laboratory research and field projects.

2. DATASETS DISTRIBUTION

The data used was based on both laboratory work and field studies that involved asphaltene bearing crude oil. The number of sources used for each type of work is shown in Table 1. The majority of the work was laboratory work, with the number of experiments reaching more than 4000 experiments involving asphaltene. Only nineteen field studies were found involving asphaltene damage and mitigation in reservoirs across the world. A study was classified as field work only if it involved a real field study or application, and thus simulation work was not included under field studies.

Table 1. Data Set Distribution

Type of Study	Number of Sources
Laboratory Studies	219
Laboratory Experiments	More Than 4000
Field Studies	19
Total Number of References Collected	250
Total Number of References Used	168

3. DATA PROCESSING METHODOLOGY

Two statistical analysis tools were used for the data processing. These tools include boxplots and histograms. Before applying these tools however, the data collected was analyzed and cleaned in order to undergo the data analysis correctly. Data analysis and cleaning process involves homogenizing the units for each data set in order to plot the values together and determining outliers that may affect the distribution and analysis of the data negatively since they have no relation to the data set. Data processing is extremely important since without this procedure, inaccurate information may be conveyed in the histograms and the boxplots.

3.1. BOXPLOT

Figure 1 provides an illustration of a conventional boxplot. A boxplot is a statistical analysis tool that divides the data into five distinct sections, including the maximum value, represented as the upper bar, third quartile range (75th percentile), represented as the upper box, the median value (50th percentile), represented by the middle line, first quartile range (25th percentile), represented by the lower box, and the minimum value, represented as the lower bar. The mean of the data is also shown on the plot as the cross-mark. A boxplot can provide an indication of how well the data is distributed within each quartile range. It can also show the minimum and maximum data point available. Boxplots are usually compared to each other in order to compare the distribution of different datasets together and their maximum and minimum values. They can also be used to compare different cases to each other, such as comparing laboratory experiments to actual field tests. This helps differentiate between different cases and offers a good idea on the difference in data between the different conditions.

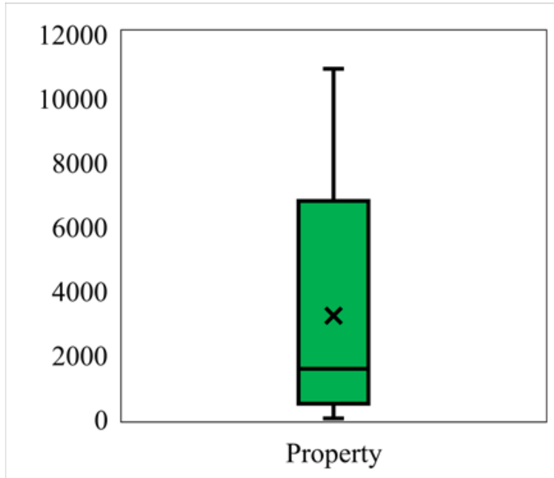


Figure 1. Boxplot Illustration

3.2. HISTOGRAM

Figure 2 provides an illustration of a conventional histograms. They help determine the frequency at which a specific range of data are repeated in the dataset. Histograms can therefore define the minimum and maximum frequency ranges, and are extremely useful, especially when developing a screening criterion. In all the histograms presented in this research, the highest frequency range will be illustrated in orange, and the lowest frequency range will be illustrated in blue. All other frequency ranges will be shown in green.

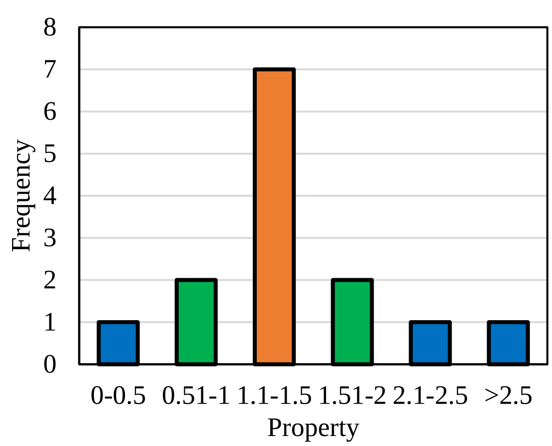


Figure 2. Histogram Illustration

4. RESULTS AND ANALYSIS

The data analysis is divided into laboratory dataset results, and field set results. The laboratory dataset includes references related to chemical analysis, mathematical modeling, numerical simulation, and core flooding experiments. The field data set includes only references that reported an actual field test or case, and does not include simulation results.

4.1. LABORATORY DATASET RESULTS

Both histograms and boxplots have been generated for the laboratory data sets. The histograms and boxplots include asphaltene properties, heteroatoms concentration, crude oil properties, thermodynamic conditions, and core flooding properties. Figure 3 shows a pie chart for the distribution of data included in the laboratory dataset. The majority of the data falls within the chemical analysis section, while only 12% of the data represents core flooding.

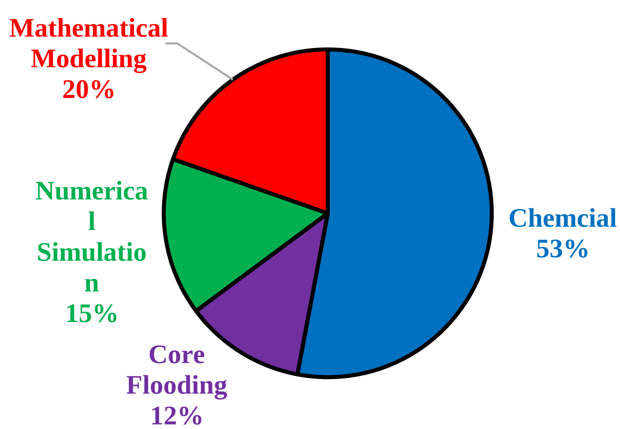


Figure 3. Laboratory Results Distribution

4.1.1. Asphaltene Properties Histograms. The asphaltene properties presented in this research are the asphaltene concentration and asphaltene molecular weight. The asphaltene concentration in the crude oil affects asphaltene stability and its likability to precipitate from solution significantly (Barrera, D.M. et al., 2013; Castro, L.V. and Vazquez, F., 2009; Ciminu, R. et al., 1995; De Boer, R.B. et al., 1995)). The asphaltene molecular weight will influence the overall oil molecular weight since asphaltenes are extremely high molecular weight components. Figure 4 shows the histograms for both the asphaltene concentration, and the asphaltene molecular weight. Based on the asphaltene concentration histogram, it can be observed that the asphaltene concentration in oil can reach extremely high levels, above 25%, even though it was the least frequency range. The highest frequency range was observed to be between 1.1 to 5 wt%, which is considered a moderately low asphaltene concentration, although it can still pose a serious threat during production due to the large volumes of oil produced. Asphaltenes are considered one of the highest molecular weight components in the crude oil, and thus the histogram for the molecular weight shows large values, with the highest frequency range being 1000.1- 2000 g/mol.

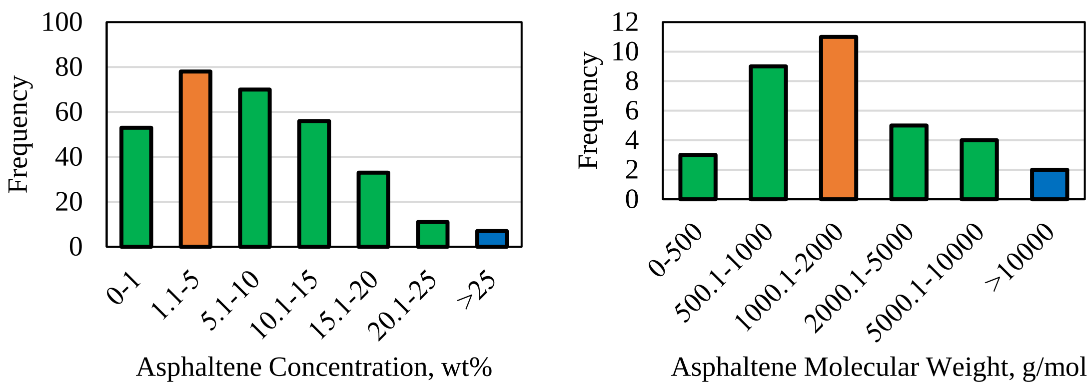


Figure 4. Asphaltene Properties Histograms

4.1.2. Heteroatoms Concentration Histograms. Heteroatoms are any atoms in the hydrocarbon ring that are not carbons. The three most common heteroatoms associated with asphaltenes are nitrogen, oxygen, and sulfur. The presence of a relatively higher than normal concentration of any, or all, of these heteroatoms gives a strong indication of the presence of asphaltene in the crude oil. Figure 5 shows the histograms for the nitrogen and oxygen content in the crude oils associated with asphaltene found in the literature. Both histograms show the presence of nitrogen and oxygen in almost all the cases where asphaltenes were reported, with some exceptions. The nitrogen content is smaller than that of the oxygen due to the overall low concentration of nitrogen in the crude oil compared to oxygen, however, the presence of both them, even at low concentrations is a good indication of the presence of asphaltene. Figure 6 shows the histogram for the sulfur content in the crude oil. Asphaltenes are usually associated with a large concentration of sulfur, which is evident from the histogram results, with the highest frequency range being between 4.1-5 wt%. The difference of concentration of the heteroatoms depends on the asphaltene concentration in the crude oil, the structure of the asphaltene, and the overall composition of the crude oil. Since all three of these conditions may vary significantly, a variety of concentrations are observed from different cases. Bahman et al. (2017) showed the range of heteroatom concentration in asphaltene based on the results from 57 different oil samples. They found that the oxygen ranged from 0.3-4.9%, the nitrogen ranged from 0.6-3.3%, and the sulfur ranged from 0.3-10.3%, all of which fall within the ranges presented in the histograms. The main difference is that this research provides a more comprehensive range of oil sample.

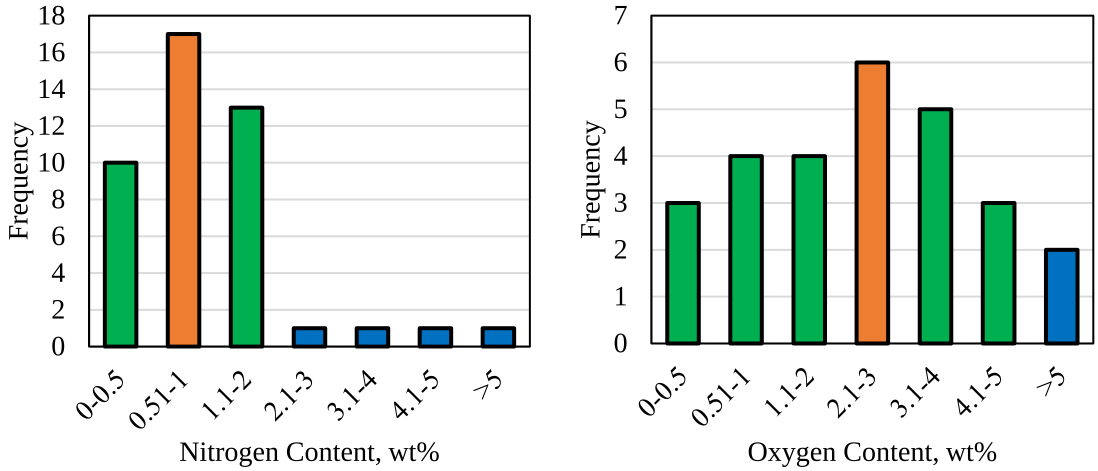


Figure 5. Nitrogen and Oxygen Content in Asphaltene Histograms

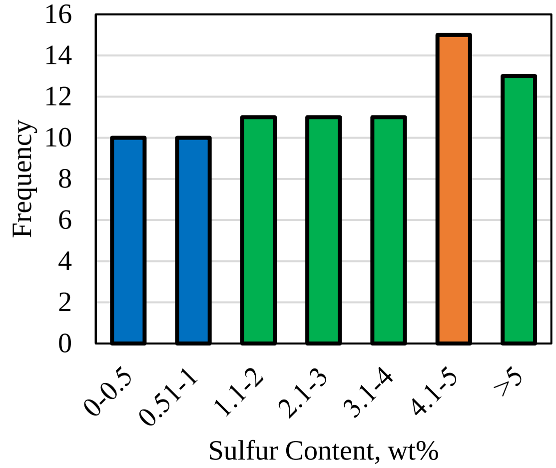


Figure 6. Sulfur Content in Asphaltene Histogram

4.1.3. Crude Oil Properties Histograms. The histograms for the crude oil generated in this research include oil molecular weight, oil viscosity, oil specific gravity, and oil API gravity, presented in Figure 7. The oil molecular weight histogram shows ranges with values much lower than that of the asphaltene molecular weight, which shows the extent to which asphaltene molecular weight is higher compared to the overall crude oil. The oil viscosity frequency plot covers an extremely broad range, which is an indication that asphaltenes can occur in any type of oil. The main difference is the asphaltene concentration in the oil with the lower viscosity oils generally having a lower asphaltene concentration than the higher viscosity oils, as was indicated in the Yen-Mullins model (Mullins, O.C., 2011). The majority of the oils reported had a moderate API gravity value, and therefore a relatively average specific gravity as well, since both are related.

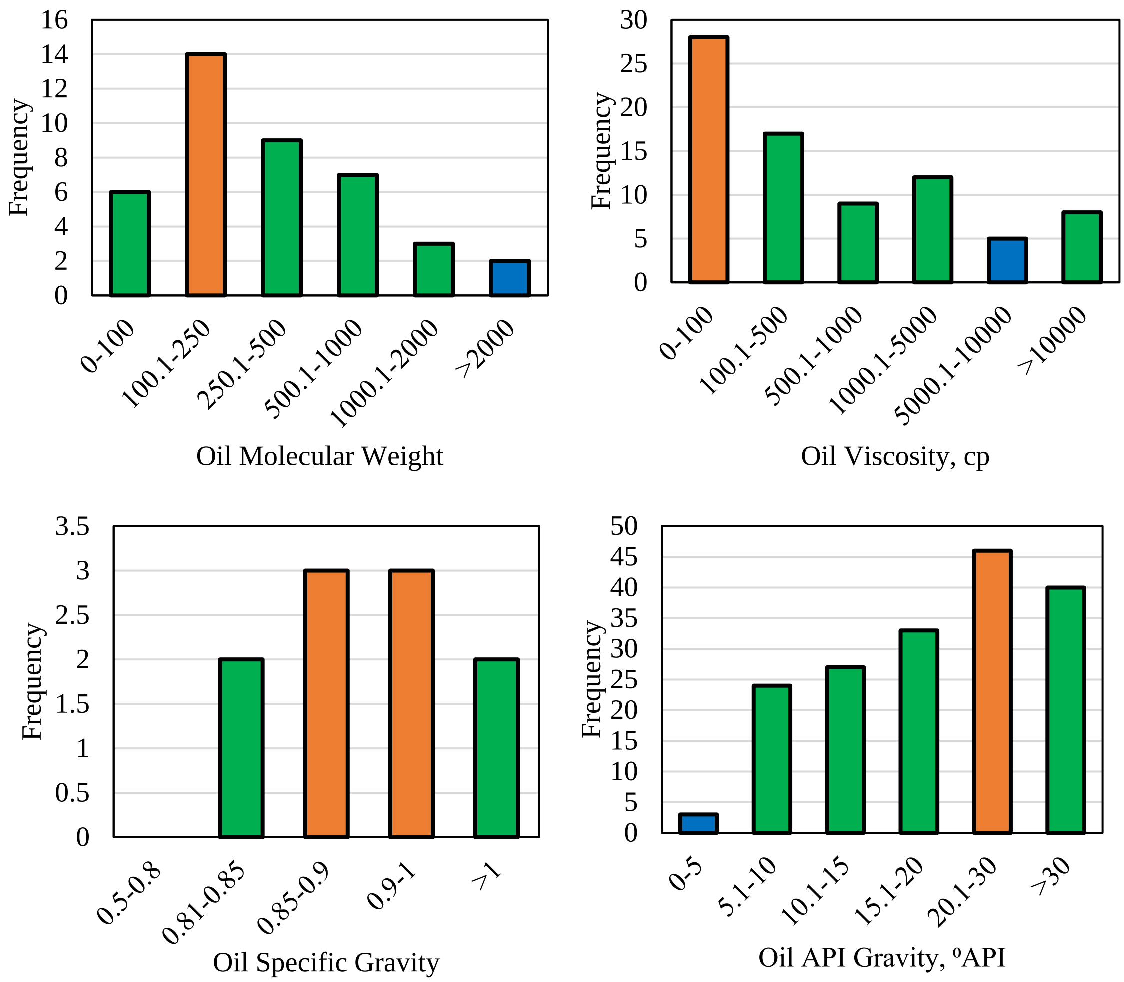


Figure 7. Crude Oil Properties Hisotgrams

4.1.4. Thermodynamic Conditions Histograms. Thermodynamic conditions include temperature and pressure. Both these parameters have a strong impact on the asphaltene stability in crude oil (Arciniegas, L.M. and Babadagli, T., 2014), and thus it was important to include them in the data analysis. Figure 8 presents the histograms for the thermodynamic conditions. The highest frequency ranges for both parameters is within the lower values. This is mainly due to the majority of the studies focusing on chemical analysis rather than flooding experiments.

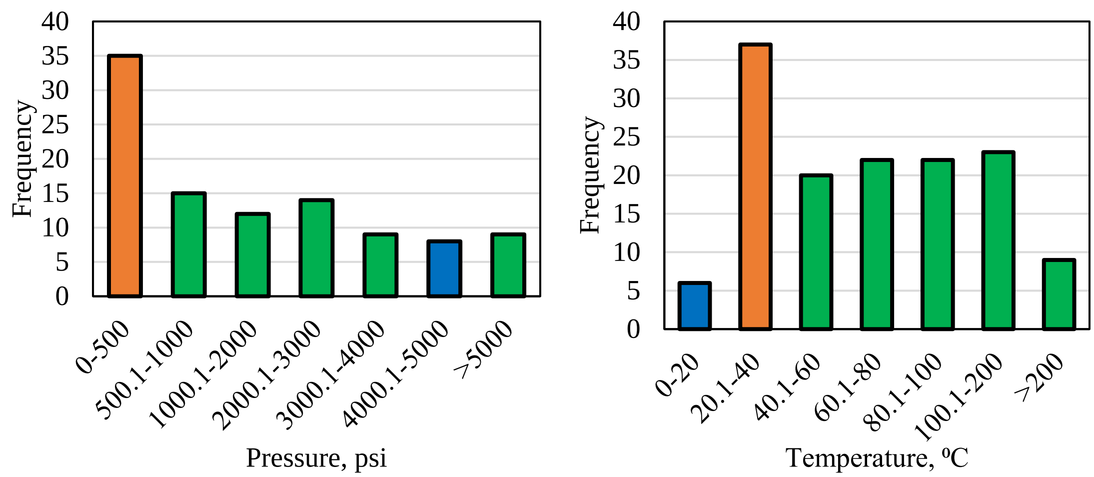


Figure 8. Pressure and Temperature Histograms

4.1.5. Core Flooding Properties Histograms. Different types of formations have been investigated for asphaltene pore plugging in the lab. These formations not only include common lithologies such as sandstones and carbonates, but also some researchers have used glass beads, and composite cores composed of different types of lithologies. Figure 9 shows the different lithologies that were used to investigate asphaltene pore plugging. The majority of the cores used were either carbonates, or calcites, mainly manifested in sand. The highest porosity and permeability experiments were the ones that used sand packs and glass beads. The shale experiments were mainly form shale cores from the USA, while the carbonates were mainly from the Middle East. The core flooding parameters investigated in this research are mainly related to the core properties since the thermodynamic properties were covered previously. The core properties investigated include the core permeability, porosity, length, and diameter. Figure 10 shows the histograms generated for all four core properties. The majority of the cores used had a diameter of 1.1-1.5 inches, and a length of 1-5 inches. The permeability was mostly in the lower ranges as well as the porosity. This is mainly due to the nature of the study, which involves asphaltene pore plugging, which was reported to be much more severe in the lower permeability (Fakher, S. and Imqam, A., 2018b; Shen, Z. and Sheng, J., 2018). This is mainly due to the fact that the smaller pores will plug up much faster than the larger pores and thus the oil recovery will be affected in a much more rapid way. Also, since the capillary pressure in the smaller pores is much higher, the flow of fluids through these pores is much more difficult compared to the larger pores, which makes the overall production from the smaller permeability reservoirs much more difficult compared to the larger permeability reservoirs, such as conventional sandstone or carbonate reservoirs with micropores.

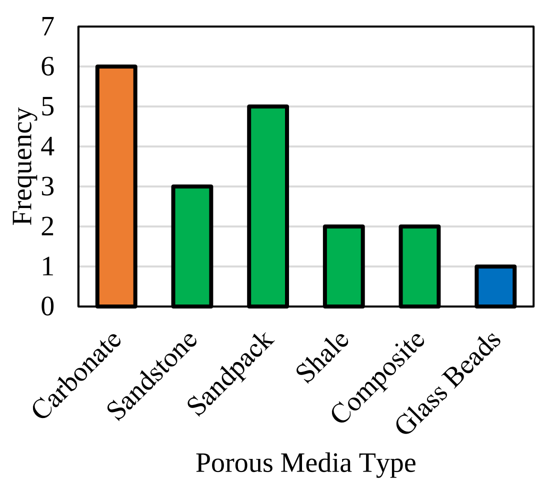


Figure 9. Porous Media Type Histograms

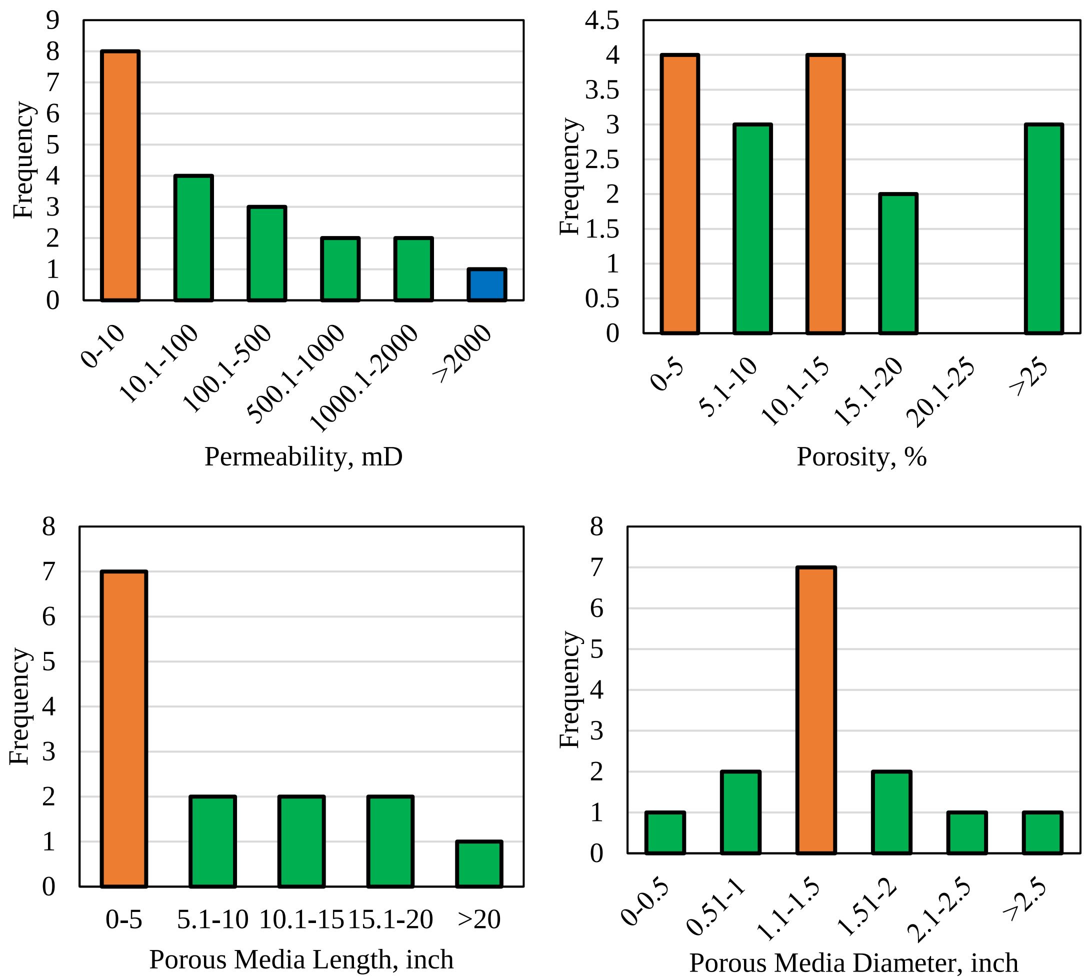


Figure 10. Core Flooding Properties Histograms

4.1.6. Asphaltene Properties. The boxplots for the asphaltene properties, including asphaltene concentration and asphaltene molecular weight, are shown in Figure 11. A maximum of 43 wt% asphaltene was found in one of the studies, which used bitumen as the hydrocarbon. The asphaltene molecular weight was mostly in the lower values, which is evident from the size of the first quartile range box. Since the size of the first quartile range is small, the distribution of the data in this quartile is relatively well. The median value is also closer to the first quartile range.

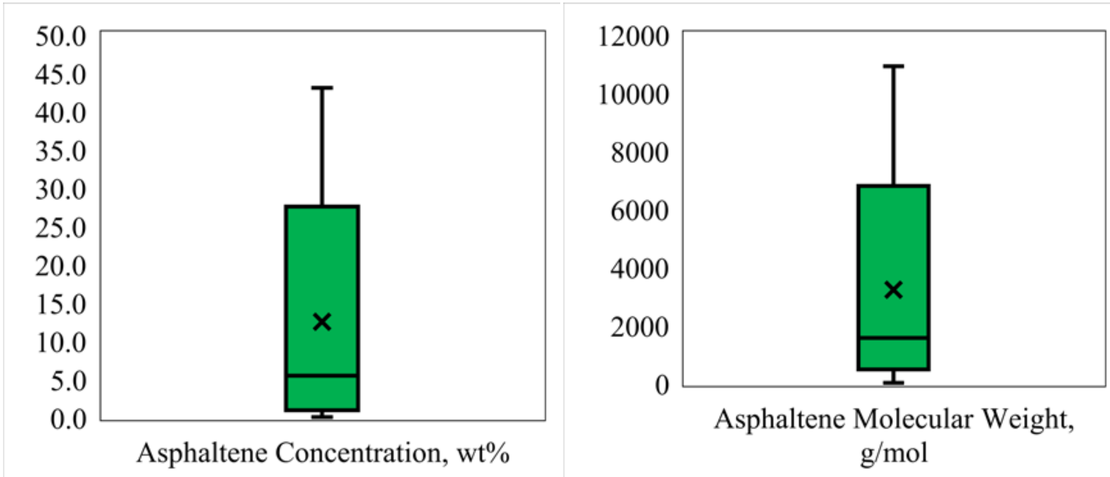


Figure 11. Asphaltene Properties Boxplots

4.1.7. Heteroatoms Concentration Boxplots. The boxplots for the heteroatoms associated with asphaltene are shown in Figure 12 and Figure 13. Based on the y-axis, the sulfur content is the highest, then the oxygen, and finally the nitrogen. The presence of heteroatoms with the relative concentrations observed in the boxplots is a strong asphaltene indicator.

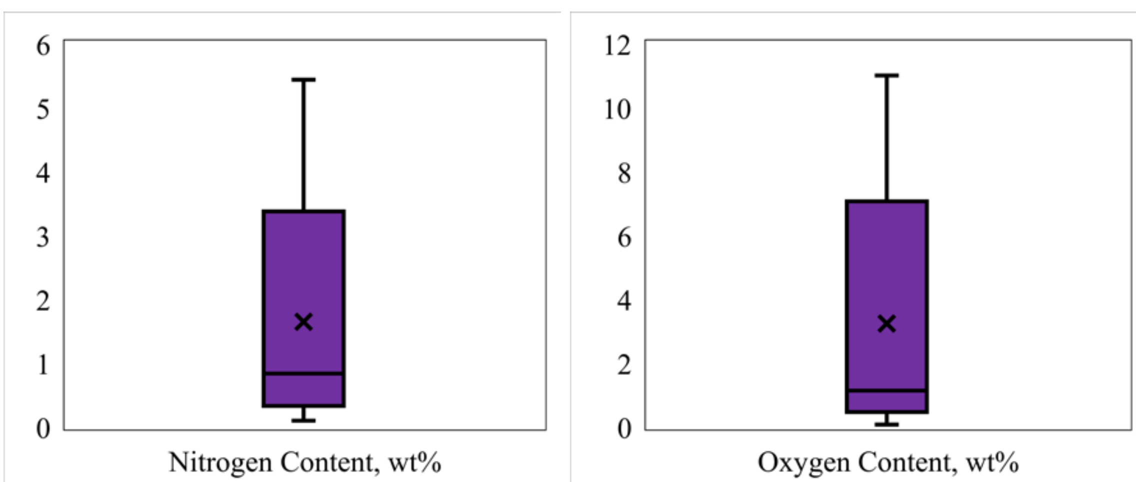


Figure 12. Nitrogen and Oxygen Content in Asphaltene Boxplots

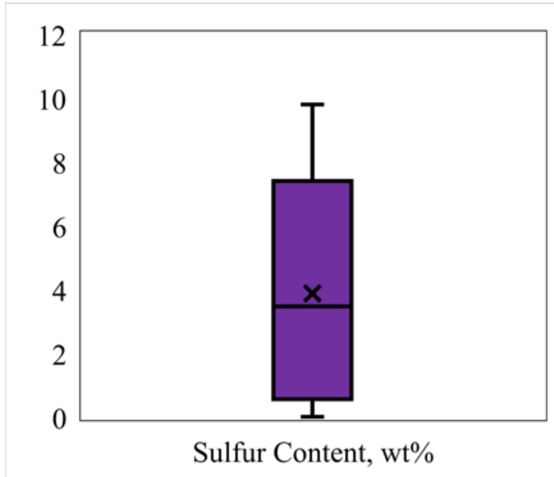


Figure 13. Sulfur Content in Asphaltene Boxplot

4.1.8. Crude Oil Properties Boxplots. Figure 14 shows the boxplots generated for the crude oil properties. Based on the boxplots, an extremely wide range of oil properties may bear asphaltenes within them. Oil viscosity as low as 1 cp, or even lower, and API gravities as high as 50 ^{0}API have been reported to have an asphaltene concentration. This shows the importance of studying asphaltenes since they are a component that can be present in any type of crude oil regardless of its properties. The oil molecular weight of 7800 g/mol, and specific gravity larger than 1 was for the bitumen, which is considered an extremely heavy oil. Compared to the asphaltene molecular weight ranges, shown previously, the oil molecular weight is much lower. This indicates two significant things, including that the asphaltene presence in the crude oil and its concentration plays a significant role in impacting the overall oil molecular weight, and from this, the oil molecular weight becomes it itself a strong indicator of asphaltene presence. If the oil molecular weight is extremely high, then there must be components within it that are impacting its molecular weight. These components will have an extremely high molecular weight themselves, such as asphaltene, which in turn will impact the overall molecular weight of the oil. By this, an indication of asphaltene in the crude oil can be determined from the crude oil properties.

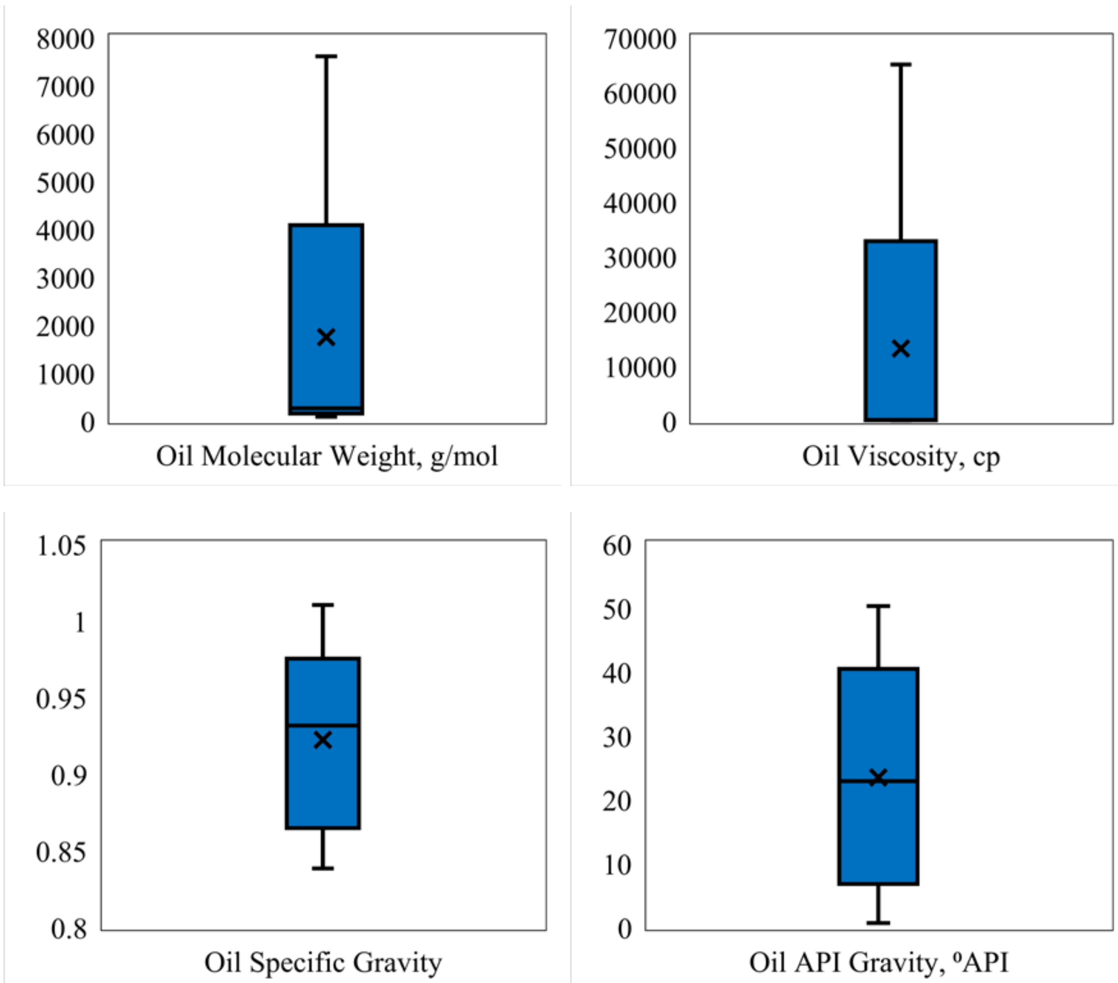


Figure 14. Crude Oil Properties Boxplots

4.1.9. Thermodynamic Conditions Boxplots. The boxplots for the pressure and temperature conditions are shown in Figure 15. Based on the conditions at which the crude oil is being produced, including normal production or solvent injection, asphaltene may begin to precipitate. Pressure and temperature conditions will either facilitate or hinder the precipitation of asphaltene based on production method. The boxplots show that asphaltene may begin to form at an extremely wide pressure and temperature range, which is mainly due to the fact that asphaltene precipitation is a function of many parameters, including, but not limited to, thermodynamic conditions of the reservoir (Ashoori, S. et al., 2010; 2017).

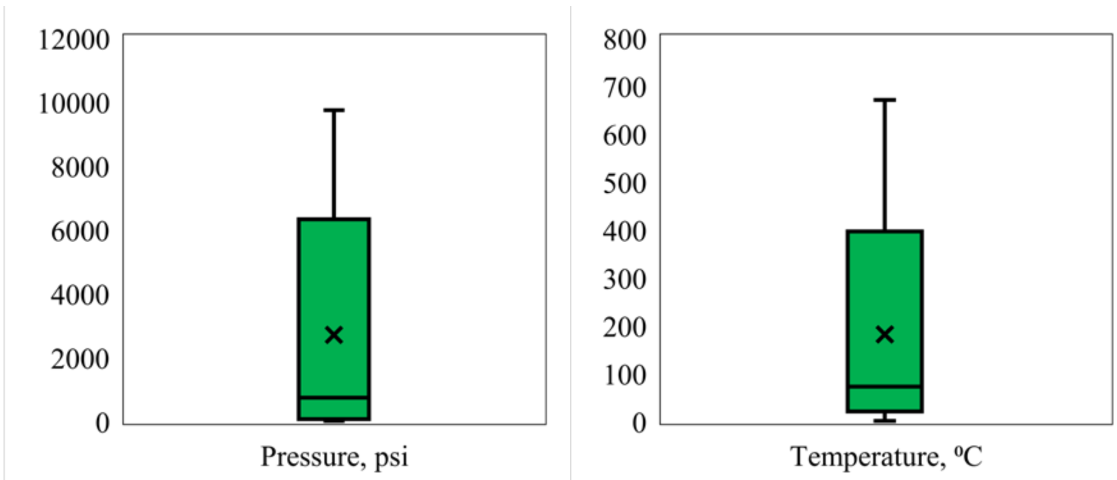


Figure 15. Pressure and Temperature Boxplots

4.1.10. Core Flooding Properties Boxplots. The boxplots for the core flooding properties are presented in Figure 16. Since different core types, and models such as sand packs and glass beads were used, large permeability and porosity values were found. The lower box in the permeability boxplot is not easily distinguishable for two main reasons including the good level of distribution of data within this quartile, and also the majority of the data is present within this quartile, which is also evident due to the closeness of the median value to this quartile. Other core flooding parameters may also play a significant role in asphaltene damage. These may include the pore size heterogeneity, presence of natural fractures, and the mineralogy of the core itself , even if they have the same lithology or rock type.

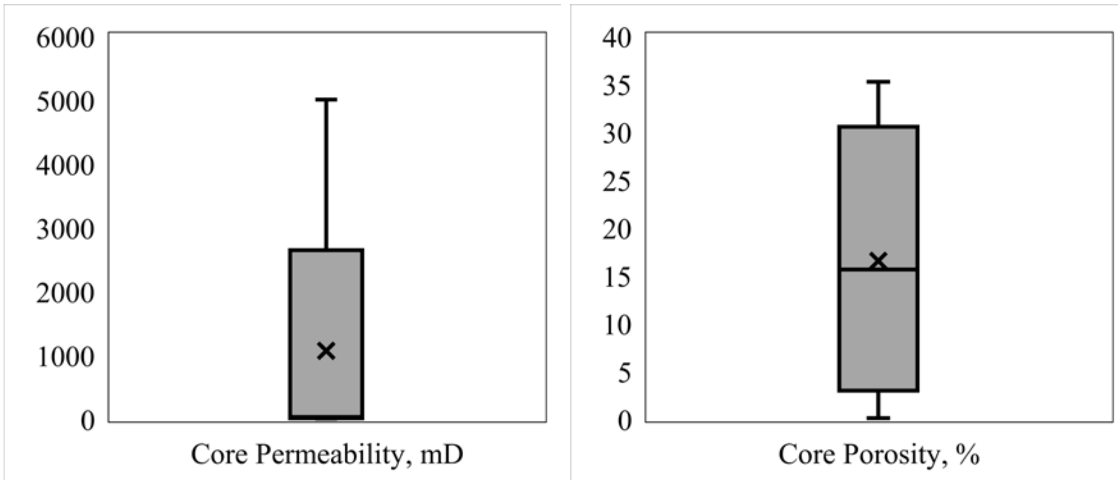


Figure 16. Coreflooding Properties Boxplots

4.2. FIELD DATASET RESULTS

The field dataset results will include histograms and boxplots for 19 case studies involving asphaltene worldwide. The statistical analysis will include asphaltene, oil, thermodynamic, and rock properties. The 19 field studies include different countries worldwide, with the majority of the case studies located in the USA and Middle East, as shown in Figure 17. A histogram is also presented, showing the distribution of field cases.

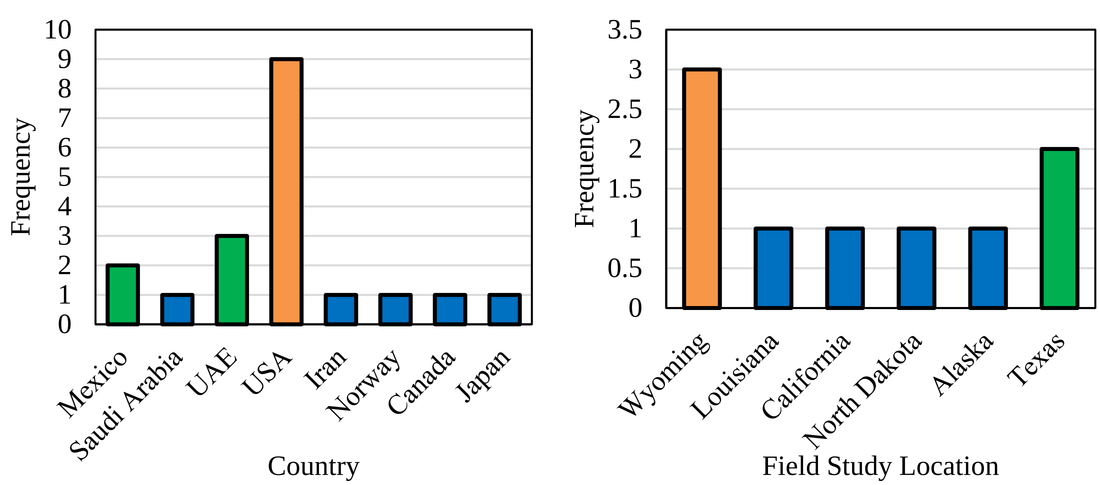


Figure 17. Field Locations Histograms

4.2.1. Asphaltene Properties Histogram. The asphaltene concentration histogram is shown in Figure 18. The highest frequecny range observed was the lowest range in the histogram. The difference between the highest and lowest frequency ranges is only in three studies however. This is mainly due to the limited data published on fields associated with asphaltene problems due to some data being restricted and thus unpublishable. The asphaltene concentrations observed in the field studies however are much smaller than thoses reported in the laboratry experiments.

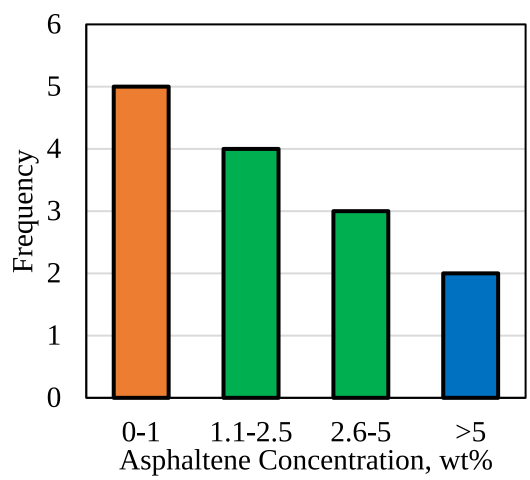


Figure 18. Asphaltene Concentration Histogram

4.2.2. Oil Properties Histogram. The oil API histogram is shown in Figure 19. Only the oil API is presented in the oil properites due to limited data in field studies. Most of the oil used is considered light oil, with an API Gravity of 30.1-40 ^{o}API. No field studies reported oils with 5-10 and 20.1-30 ^{o}API, which is due to the limited data avaliable for the fields due to restrictions, in comparison to laboratorty work, which is generally more avaliable. Even though the data included in field cases is limited, the histogram still covers a wide range of oil API gravities between 10.1- more than 40 ^{o}API.

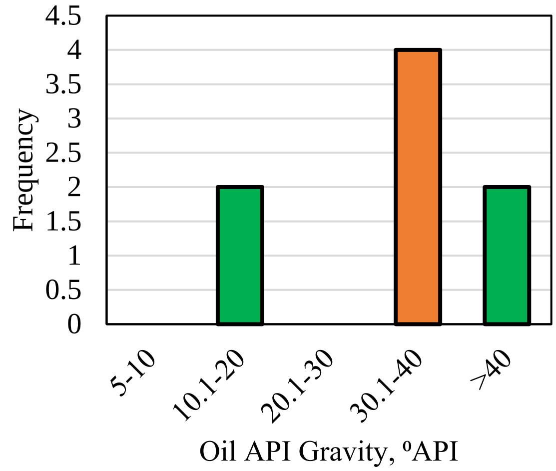
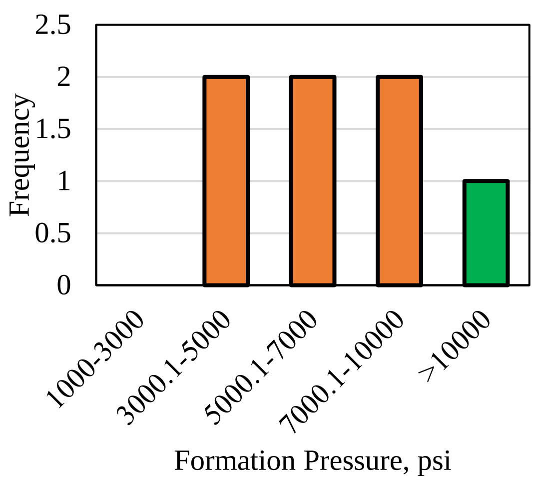


Figure 19. Oil API Gravity Histogram

4.2.3. Thermodynamic Properties Histograms. The formation pressures and temperatures reported in the field studies are presented in the hisotgrams in Figure 20. A wide range of pressures were reported, while the temperatures reported ranges from 50-200 °C. Some of the ranges have no data within them mainly due to the lack of data reported. Temperatures above 200 °C were not reported, although temperatures in the laboratory results reached up to 670 °C.



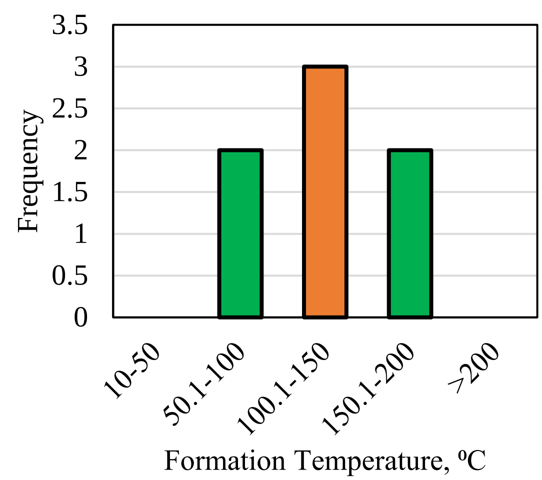


Figure 20. Thermodynamic Properties Histograms

4.2.4. Rock Properties Histograms. The rock properties histograms include pay zone depth and the rock type. Figure 21 shows the results for both histograms. The majority of the studies reported a carbonate formation, as was the case in the lab studies. Most of these carbonate reservoirs were limestones located in the Middle East or the United States. A pay zone depth of 5000.1- 10000 ft had the highest frequency of all the ranges reported in the literature. This depth is considered not too deep, and also not too shallow compared to the range between 1000.1-2000 ft, and the range between 10000.1-15000 ft, and greater, which are considered relatively shallow and deep respectively. Two of the ranges found within the histogram had no data within them but it was still important to include them to increase the accuracy and integrity of the histogram generated.

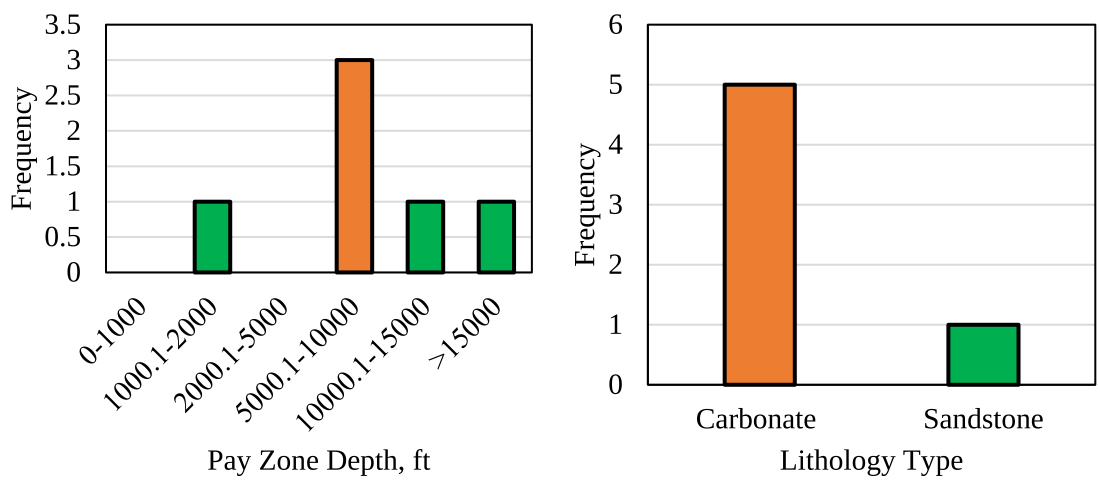


Figure 21. Rock Properties Histograms

4.2.5. Asphaltene Treatment Method Histogram. Several researchers have investigated many techniques to mitigate asphaltene precipitation and deposition. All the methods used can be grouped into two broad caterogiers. These catergories include chemical methods, which involoves the injection of any chemical inside the wellbore or the reservoir to disolve the asphaltene and homogenize it within the crude oil again, and mechanical methods, which include any mechanical or mechanical-based method such as directly drilling the asphaltene or water-jetting. Figure 22 shows the frequency plot for the chemical and mechanical mitigation attempts in fields from different countries worldwide. Based on the histogram, the majority of the fields attempted the use of chemcials, some of which are extracted components of the crude oil such as toluene or xylene while others are extracted from other sources such as plants, rather than mechanical methods. It should be noted that the use of a specific technique is highly dependant on many factors including the reservoir thermodynamics, fluid and rock type, strucutre and concentration of the asphaltene, and the degree of asphaltene plugging or damage at the time of treatment. Also, the use of chemicals is highly based on environemental regulations, compatiability of the chemical with the reservoir and crude oil, and avalibility of the chemcial.

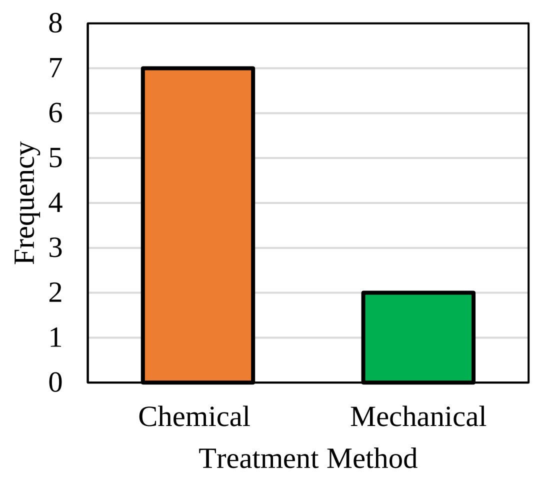


Figure 22. Treatment Method Histogram

4.2.6. Asphaltene Properties Boxplot. The boxplot for the asphaltene concentration is presented in Figure 23. The highest asphaltene concentration reported was

14 wt%, which is considered a high percentage, although higher values were observed in the laboratory results. The majority of the data reported lies within the lower values, based on the size of the lower box and the median bar in the boxplot. Also, the distribution of the data in the upper box is considered highly uneven, which is evident from the size of the box compared to the lower one.

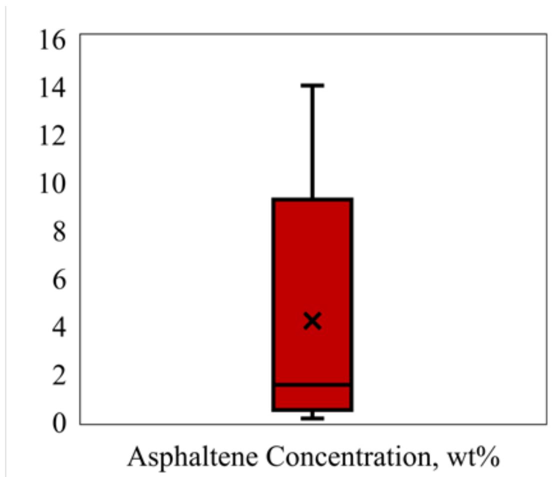


Figure 23. Asphaltene Concentration Boxplot

4.2.7. Oil Properties Boxplot. The boxplot generated for the oil API gravity is shown in Figure 24. The highest API gravity found was 41.2 ^{o}API, which is considered light oil, while the lowest value was 12 ^{o}API, which is slighlty lighter than heavy oil. The majority of the data lies within the higher values however, which indicates that most of the field studies were reported on light oils. The distribution of the data within the first quartile range, indicated by the lower box, is highly uneven. This is indicated by the size of the box relative to the third quartile range, indicated by the upper box. The oil API Gravity is an extremely important parameter that will govern the quality of the crude oil, and its overall selling cost.

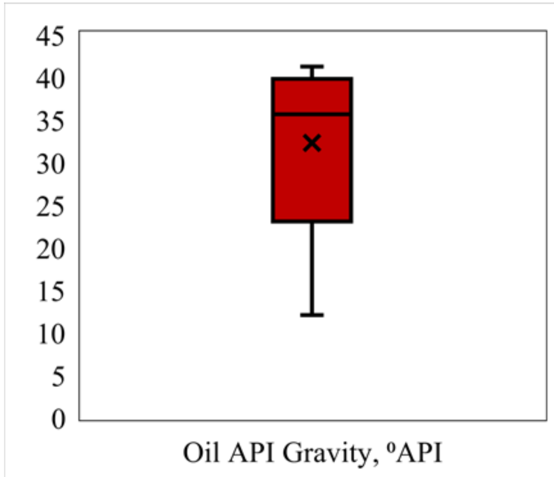


Figure 24. Oil API Gravity Boxplot

4.2.8. Thermodynamic Properties Boxplot. The thermodynamic properties, including pressure and temperature, boxplots are shown in Figure 25. The pressures recorded reached 13103.7 psi. The third quartile range for the pressure boxplot is less evenly distributed compared to the first quartile range. Also, the median value is closer to the first quaritle range which indicates that the majortiy of the data lies within this range. The highest reservoir temperature reached 200 °C, while the lowest reported was 56 °C.

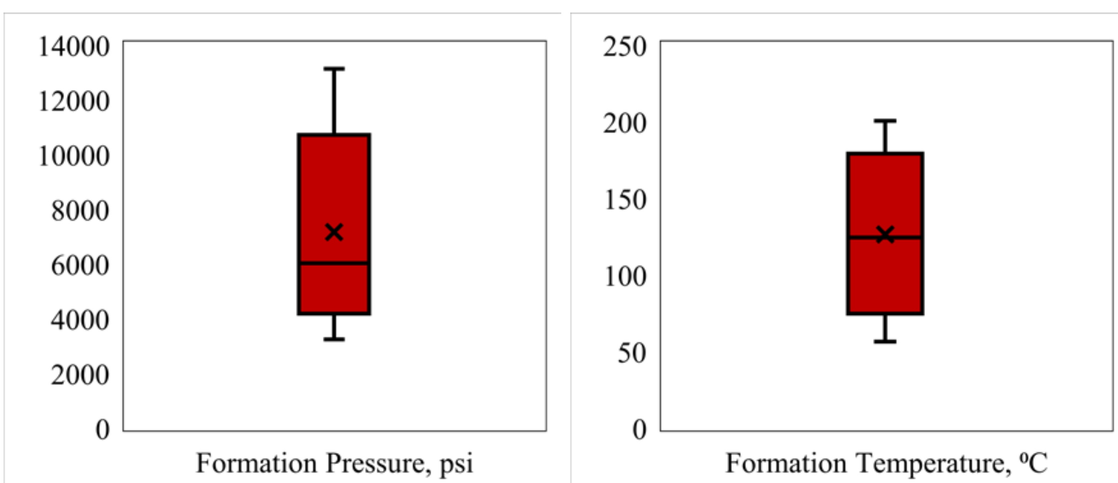


Figure 25. Thermodynamic Properties Boxplot

4.2.9. Rock Properties Boxplot. The pay zone depth boxplot is presented in Figure 26. The highest depth recorded was close to 20000 ft, with the distribution of the data beiing less even compared to the lower range. The average and median values are closer to the lower range, whereas the mean value lies within the third quartile range. This indicates that more data lies in the first quartile range, but the values in the thrid quartile range are much higher compared to the first quartile range, and thus the mean is slightly larger than the median value.

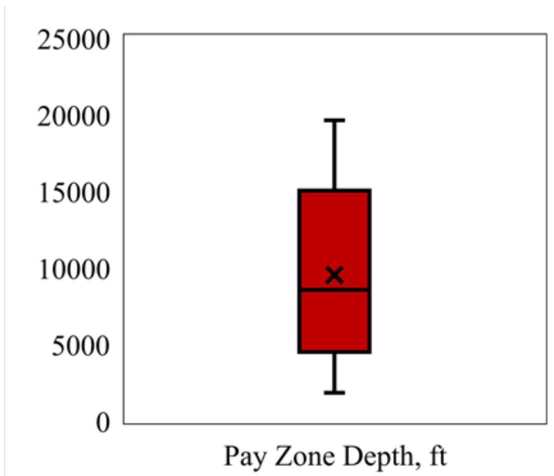


Figure 26. Pay Zone Depth Boxplot

5. DATA RANGES FOR FIELD AND LABORATORY RESULTS

Based on the histograms and boxplots generated for both the laboratory and field studies, it was evident that the values from both were not similar in almost all cases. It is therefore important to differentiate between both of them. Table 2 provides a summary of the data found for both the laboratory and field studies in order to compare both. Only the data that was available for both the field and the lab will be included in the table. The asphaltene concentration, API gravity, and temperature values in the lab are higher than those in the field, whereas the pressure in the field was higher than the lab. The highest frequency lithology in both was carbonate rock, mainly limestone. This table can help determine the best ranges for experimental work on asphaltene, either based on chemical analysis or core flooding experiments. The table can also help researchers correlate between values found in the field with their experiments to mimic field conditions. This table is limited however to the properties mentioned within it. This is mainly due to the lack of reported data on some major parameters, especially for the field results, since most of the field data is considered confidential. The table still provides a comparison of some parameters, and works to illustrate the difference between field and lab results.

Table 2. Comparison of Laboratory and Field Data

Study	Parameter	Max	Min	Median	Highest Range	Lowest Range
Lab	Asphaltene Concentration	43	0.01	5.4	1.1-5	>25
	Oil API Gravity	50.21	0.6	22.8	20.1-30	0-5
	Pressure	9727	14.7	725.1	0-500	4000.1-5000
	Temperature	670	0	71.4	20.1-40	0-20
	Lithology	-	-	-	Carbonate	Glass Beads
Field	Asphaltene Concentration	14	0.1	1.5	0-1	>5
	Oil API Gravity	41.2	12	35.6	30.1-40	5-10 20.1-30
	Pressure	13103	3218	6000	3000.1-10000	1000-3000
	Temperature	200	56	124	100.1-150	10-50 >200
	Lithology	-	-	-	Carbonate	Sandstone

6. CONCLUSIONS

A comprehensive data analysis was performed on both laboratory and field studies involving asphaltene. The factors impacting asphaltene stability were included in both the histograms and the boxplots, along with the asphaltene concentration reported in laboratory and field studies to provide a guideline to the conditions at which asphaltenes may precipitate and cause pore plugging during both lab experiments, and field work. A comparison was also provided between some of the lab and filed data to determine the ranges at which both can be studied effectively.

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APPENDIX

This appendix includes all the references that were used to perform the data analysis in the research paper

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II. ASPHALTENE PRECIPITATION AND DEPOSITION DURING CO2 INJECTION IN NANO SHALE PORE STRUCTURE AND ITS IMPACT ON OIL RECOVERY

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ABSTRACT

Carbon dioxide (CO_2) injection has been shown to improve oil recovery from conventional oil reservoirs, with a relatively high rate of success. Recently, it has also been applied in unconventional shale reservoirs, with hopes that it could improve oil recovery from them as well. The process proved successful in some shale plays, but failed in others. This research investigates the CO_2 flow mechanism in nano-pores and its impact on asphaltene precipitation, which could lead to pore plugging and a reduction in oil recovery. Nano-composite filter membranes were used to conduct all experiments. The setup used was a specially designed filtration apparatus that could incorporate the nano filter membranes. The factors studied include the CO_2 injection pressure, temperature, oil viscosity, CO_2 soaking time, porous media thickness, nano-pore size, and pore size heterogeneity. Asphaltene wt% was quantified for all the experiments, both for the produced and bypassed oil. Increasing the CO_2 injection pressure resulted in a higher oil recovery and a shorter CO_2 breakthrough time. Also, the percentage of asphaltene in the recovered oil was higher for the higher CO_2 injection pressure. Results indicated that increasing the temperature also resulted in a higher oil recovery, however, the asphaltene wt% in the bypassed oil also increased with temperature due to instability of the oil stabilizing agent, resin. It was found that the higher oil viscosity had a larger asphaltene

weight percent. Increasing the thickness and heterogeneity resulted in a decrease in oil recovery and also a higher asphaltene weight percent. Increasing the nano-pore size resulted in a significantly higher oil recovery, and less pore plugging. This research investigates the flow mechanism of CO_2 injection and asphaltene precipitation due to CO_2 injection in nano-pores in order to better understand the main factors that will impact the success of CO_2 injection in unconventional shale reservoirs.

1. INTRODUCTION

Carbon Dioxide injection is an enhanced oil recovery (EOR) technique applied in hydrocarbon reservoirs to increase oil recovery. CO_2 injection has been applied extensively in conventional oil reservoirs with a high success rate (Meng, X. et al., 2017). Very recently, several pilot tests have been conducted to investigate the applicability of CO_2 injection in unconventional reservoirs, and the extent to which it can improve oil recovery (Rassenfoss, S., 2017). The exact mechanism and flow regime by which the CO_2 flows in the nano-pores of the shale reservoirs is not yet fully understood (Sheng, J. and Chen, K., 2014; Sheng, J. et al., 2015; Wang, S. et al., 2016; Li, L. and Sheng, J., 2017). Another major point that has not been fully investigated for CO_2 injection in nano-pores is asphaltene precipitation which can deposit in these nano-pores and result in pore plugging which can reduce oil recovery and cause severe operational problems (Shen and Sheng, 2018).

Several researchers have studied the application of gas injection in shale reservoirs. Kang, S. et al. (2011) evaluated CO_2 adsorption to the shale rock using the application of volume and mass balance equations. Their work was concerned with CO_2 storage in shale reservoirs. Gupta, N. et al. (2013) investigated the impact of shale mineralogy on oil recovery. They used Fourier Transform Infrared Spectroscopy to analyze the shale core. Flow mechanisms of multi-component systems in shale reservoirs was investigated by Fathi, E. and Akkutlu, I. (2014). They developed a new mathematical model based on the Maxwell-Stefan Formulation to simulate the flow. The main drawback of their model was that it did not take into account the shale mineralogy difference, and therefore had limited applicability. Sheng, J. (2014, 2015, 2016, 2017) performed an extensive lab and simulation study to evaluate the effect of different gas injection mechanisms, including gas injection and gas huff-n-puff on oil recovery from shale reservoirs. Their work was focused mainly on oil recovery rather than CO_2 flow mechanism. Wan, T. et al. (2015) used Eagle Ford shale cores to study the effect of soaking time on oil recovery during huff-n-puff process. Yu, Y. and Sheng, J. (2016) used nitrogen as an injection gas during huff-n-puff to investigate the effect of soaking time, and pressure on oil recovery. Li, L. and Sheng, J. (2017) then evaluated the use of methane as an injection gas, instead of nitrogen, for huff-n-puff application. Fragoso, A. et al. (2015) performed a simulation study on gas EOR in shale reservoirs using a dual porosity, dual permeability model to evaluate the performance of several gases on oil recovery. Kim, T. et al. (2017) also performed a simulation study, but integrated the Extended Langmuir Isotherm in their model to account for gas adsorption, for more realistic results. Jin et al. (2017) showed that CO_2 flow in the nano-pores of the shale mainly falls under Free Molecular Flow behavior using the Knudsen Number definition of flow regimes. This indicated that the flow of CO_2 in the nano-pores is mainly diffusion dominated. The majority of the research work discussed focuses on oil recovery increase in unconventional reservoirs only, however, very few researches have investigated asphaltene deposition in unconventional reservoirs.

Much research has been conducted to investigate asphaltene deposition in conventional reservoirs, while limited work has been done on asphaltene deposition in unconventional reservoirs. . Soroush S. et al. (2014) showed that below CO_2 MMP, the pore plugging damage will be much lower compared to above the MMP due to the resins that stabilize the asphaltene being much more unstable above CO_2 MMP. Srivastava and Huang (1997) underwent core flooding experiments using sandstone cores, and then used Computed Tomography Scanning to visually illustrate the impact of asphaltene deposition on pore plugging and permeability reduction in the reservoir. Shedid and Zekri (2006) observed that as the rock permeability increased, the impact of asphaltene deposition on the core permeability reduction and the overall oil recovery decreased. Moradi et al. (2012) ran experiments using 0.2 µm pore size filter membrane using nitrogen and methane and concluded that asphaltene deposition was much more severe in methane compared to nitrogen.

Very little research work has been conducted to investigate asphaltene precipitation and deposition in unconventional shale reservoirs during CO_2 injection, and its impact on oil recovery. Also, all of the researches that have investigated asphaltene precipitation in unconventional reservoirs during CO_2 injection are extremely recent due to the novelty of the topic. Mohammed et al. (2017) performed a simulation study to model asphaltene deposition in low permeability reservoirs during CO_2 injection and sought to optimize CO_2 injection by suggesting cyclic CO_2 injection with brine since CO_2 is soluble in brine, hence reducing asphaltene deposition. Shen and Sheng (2018) studied asphaltene deposition in

Eagle Ford shale reservoir using cyclic gas injection. They used filter membranes of 30 nm, 100 nm, and 200 nm to study asphaltene precipitation and deposition. The experiments they conducted with the filter membranes were undergone at 50 psi and room temperature. Their core flooding experiments concluded that the increase in asphaltene deposition reduced the overall oil recovery, without focusing on the mechanism of CO_2 flow in these nano-pores.

This research investigates the flow mechanism of CO_2 in nano-pores, and the factors that will impact oil recovery from these nano-pores using nano composite filter membranes. The research then studies asphaltene precipitation and deposition due to CO_2 injection in the nano-pores and quantifies the asphaltene weight percent from both the produced oil and the bypassed oil in all experiments. The factors studied include CO_2 injection pressure, temperature, oil viscosity, CO_2 soaking time, porous media thickness, porous media pore size, and pore size heterogeneity.

2. ASPHALTENE PRECIPITATION AND DEPOSITION MECHANISM

The main components of the crude oil can be divided into saturates, aromatics, resins, and asphaltenes. At normal conditions, these components are all homogenized in solution to form the crude oil. Saturates and aromatics are nonpolar compounds, while asphaltenes are considered polar compounds since they contain heteroatoms such as nitrogen, sulfur, or oxygen. In order for these components to be held together, a bridging agent must be present. Resins contain both polar and nonpolar sites which makes them act as a good bridging agent which holds all the crude oil components together (Speight, J.G., 2004). Once any change in equilibrium conditions occurs, the forces holding these components together become severed, and thus the asphaltene, which is the solid component in the solution, begins to precipitate. Changes in equilibrium conditions may include change in pressure, temperature, addition of a solvent such as CO_2, and high oil production flowrate (Bahman, J. et al., 2017). Following asphaltene precipitation, if the conditions are suitable, asphaltene will begin to form flocculations (Hotier, G. and M. Robin, 1983). These flocculations have a high density and will thus begin to deposit in the pores of the reservoirs. Excessive deposition will result in asphaltene buildups, and eventually, pore plugging (Srivastava and Huang, 1997). Figure 1 shows the main components of crude oil and the bond severance resulting in asphaltene precipitation.

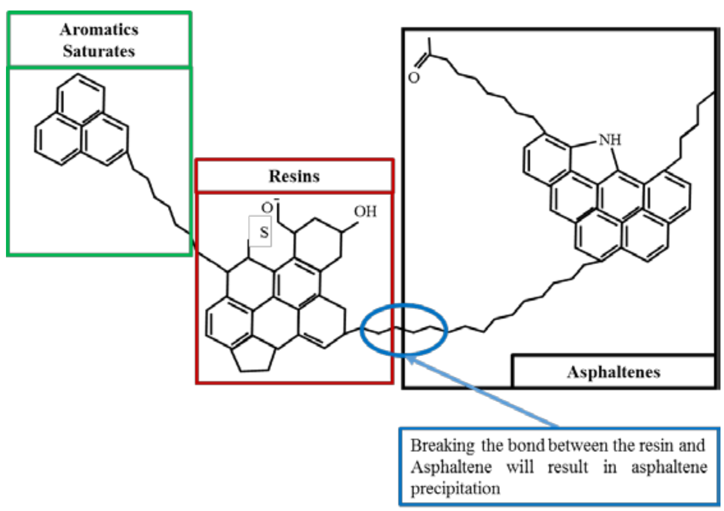

Figure 1. Main Components of Crude Oil and Asphaltene Precipitation

There are two main mechanisms by which asphaltene can precipitate and eventually deposit from the oil. These mechanisms involve either the injection of a solvent, or direct reservoir depletion. Each mechanism is explained below.

2.1. ASPHALTENE PRECIPITAION DUE TO SOLVENT INJECTION

Injecting a solvent into the formation will alter the downhole conditions of the reservoir. This will result in a disturbance in the equilibrium conditions of the reservoirs, and thus asphaltene precipitation. One of the most common solvent used is CO_2. Several factors will impact the degree of asphaltene precipitation due to CO_2 including the method of injection, either flooding or huff-n-puff, injection pressure, phase including gas, liquid, or supercritical, and miscibility, including miscible, immiscible, or near-miscible (Kokal, S.L. and S.G. Sayegh, 1995). Studying the CO_2 impact on asphaltene precipitation in shale nano-pores is the main aim of this research.

2.2. ASPHALTENE PRECIPITATION DUE TO RESERVOIR DEPLETION

Asphaltene can precipitate in the reservoir even if no solvent is introduced (Hemmati-Sarapardeh, A. et al., 2013). When producing from oil reservoirs, as the oil moves from the formation to the wellbore, the reservoir pressure will begin to drop. This pressure drop can result in asphaltene precipitation and deposition (De Boer, R.B. et al., 1995). If the reservoir pressure is initially above bubble point, asphaltene precipitation will be much more severe once the reservoir falls beneath the bubble point. If the reservoir is initially beneath bubble point, asphaltene precipitation may still occur if the production rate is high enough to result in a reduction in reservoir pressure (Nghiem, L.X., and D.A. Coombe, 1997; Kokal, S.L. and S.G. Sayegh, 1995; Hemmati-Sarapardeh, A. et al., 2013; De Boer, R.B. et al., 1995). Studying the asphaltene precipitation and deposition due to reservoir depletion alone, without solvent injection, is not the main concern of this research, and thus, will not be investigated.

3. EXPERIMENTAL MATERIAL

3.1. CRUDE OIL

Crude oil with viscosity 470, 267, and 67 cp was used to conduct the experiments. The composition of the crude oil was determined using Gas Chromatography/Mass Spectrometry, and is shown in Table 1. The chromatography is used to isolate the components of the crude oil into different fractions, while the mass spectrometry is used to quantify the fractions identified by the gas chromatography. The fractions are grouped into six major groups based on their carbon number, and the asphaltene concentration is shown on its own.

Table 1. Crude Oil Composition and Asphaltene Concentration

Component	Weight Percentage, %
C1-C5	9.37
C6-C10	14.74
C10-C15	18.89
C16-C20	19.31
C20-C30	11.63
C30+	26.06
Asphaltene (Component of C30+)	5.73
Total	100

3.2. SPECIALLY DESINGED HPHT FILTRATION VESSEL

A unique high pressure high temperature (HPHT) vessel was specially designed in the lab to be used as a filtration vessel for the oil. The vessel was designed to be leak proof and to accommodate the nano-composite filter membranes. The vessel also had a temperature regulator and a heating jacket to run high temperature experiments. The heating jacket could reach temperatures up to 300 ^{o}C.

3.3. NANO-COMPOSITE FILTER MEMBRANES

The nano-composite filter membranes used had a pore size of 0.2, 10, and 100 nm and a thickness of 0.1 mm. These sizes were used to ensure that all ranges of nano pore are covered in the research. The membranes are commercially available, and were provided as a sheet which was then cut to the desired shape based on the size of the experimental vessel, which had a 45 mm diameter.

3.4. HIGH PRECISION SCALE

A high precision, four decimal point, scale was used to weigh the asphaltene saturated filter membranes in order to obtain the weight of the asphaltene for any experiment. The high precision is required since the asphaltene weight can be very small.

3.5. CO_2 CYLINDER

A commercially available CO_2 cylinder with purity of 99.99% was used to conduct the experiments. A pressure regulator was attached to the cylinder to regulate the flow of CO_2 and to vary the CO_2 injection pressure.

4. ASPHALTENE DETECTION TEST

Asphaltenes are defined as the heavy components of the crude oil that are insoluble in n-alkanes, such as n-heptane, but soluble in aromatics such as toluene or xylene (Goual, L, 2012). Asphaltene detection is a standard procedure conducted in the industry to quantify the percentage of asphaltene in an oil sample (Jamaluddin, A.K.M. et al., 2000; Yen, A. et al., 2001). The procedure followed in this study follows the industry standard procedure used to test for Saturates, Aromatics, Resins, and Asphaltenes (SARA) (Shahriar M., 2014). The procedure involved dissolving 0.1 ml of the oil sample in 10 ml of heptane. The mixture is then vigorously stirred for one minute to ensure the complete dissolution of oil in the heptane. The sample is then left for 48 hours until all of the asphaltene precipitates at the bottom of the tube. After the asphaltene is clearly visible, the sample is filtered through a 0.45 µm filter membrane and the membrane is left to dry for another 48 hours. The membrane is weighed before and after it is used for filtration, and based on the weight difference the asphaltene weight is then determined. Finally, the asphaltene weight percent is calculated using the weight of the 0.1 ml of oil and the weight of the asphaltene on the filter membrane by applying Equation (1).

$$\text{Asphaltene wt\%} = \frac{\mathrm{wt}_{\mathrm{asph}}}{\mathrm{wt}_{\mathrm{oil}}} \times 100 \tag{1}$$

Where wt% is the weight percent, wt_{asph} is the weight of the asphaltene on the filter membrane, wt_{oil} is the weight of the oil used in the experiment.

A flow chart showing the asphaltene detection and quantification test procedure is shown in Figure 2.

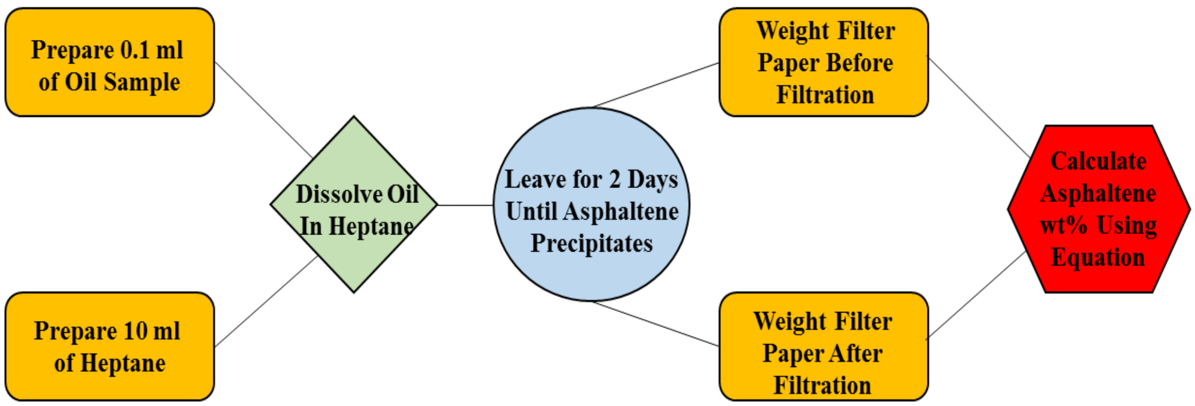

Figure 2. Asphaltene Quantification Flow Chart

5. EXPERIMENTAL SETUP

The experimental setup used to conduct the experiments is shown in Figure 3. The setup is composed of a filtration vessel which houses the oil sample and the filter membrane, a support structure with a temperature regulator which houses both the filtration vessel and the heating jacket, a CO_2 cylinder to supply the CO_2 used for the experiments, two pressure regulators to control the flow of CO_2 from the cylinder, and the CO_2 flow into the experimental vessel, and test tube to collect the oil produced. Below the filter membrane is a 60 micron mesh screen which functions to support the filter membrane, and prevent it from rupturing under high pressure. The mesh screen has a much larger pore size that the filter membrane to avoid causing any unnecessary pressure drop or hindrance to the oil flow which will affect the results. An O-ring is also present between the 60 micro mesh screen and the lower support to provide a seal and make the vessel leak proof.

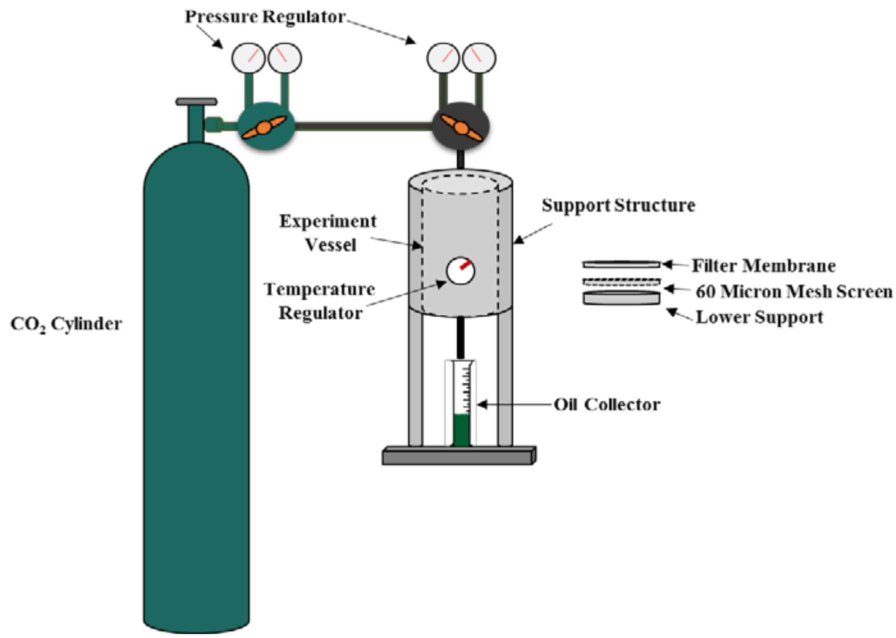

Figure 3. HPHT Experimental Setup

6. EXPERIMENTAL PROCEDURE

All experiments conducted were performed following the same procedure in order to be able to compare the results. The procedure followed is as follows:

1. Measure 30 ml of crude oil with the viscosity needed for the experiment. The oil is then poured into the experimental vessel.
2. Place the o-ring on the grooves in the vessel to provide the required seal. Place the nano filter membrane on top of the o-ring, and secure it in its place. Make sure there are no dents in the filter paper to prevent the oil from escaping through these dents during the experiment.

3. Place the 60 micron mesh screen on top of the filter membrane. The membrane will be below the screen when the experiment is run since the experimental vessel is flipped before it is placed into its support structure in order to allow the filter membrane to be on the bottom for the filtration process to take place. The 60 micron mesh screen will provide support for the filter membrane and will also prevent it from rupturing under the high CO_2 injection pressure.
4. After the 60 micron mesh screen is placed, the bottom support is sealed using six bolts to prevent any leaks. The experimental vessel is then flipped and placed in the support structure.
5. The vessel is then heated for two hours before injecting the CO_2. Following the injection of CO_2, the vessel is heated for another two hours. This is ensure that the CO_2 has had sufficient time to soak with the oil, and also to maintain the CO_2 temperature at the design temperature.
6. The vessel is then opened, and the oil is allowed to produce. The oil production is recorded every thirty seconds for the first hour, and then every minute for the duration of the test.
7. The experiment is stopped once the oil ceases to produce, and gas breakthrough occurs. The experimental vessel is then depressurized using a relief valve.
8. Both the produced oil and the bypassed oil are collected for asphaltene wt% analysis. The filter membrane is removed and sealed in a vacuum bag for further analysis as well.
9. The analysis of the filter membrane includes asphaltene quantification and solubility tests.

7. RESULTS AND ANALYSIS

Initially, the CO_2 flow mechanism in nano-pores will be explained. The oil recovery, in ml, and oil production flow rate, in ml/min for all the experiments are presented. The oil recovery percentage for all the experiments is also shown. The factors presented include CO_2 injection pressure, temperature, oil viscosity, CO_2 soaking time, porous media thickness, porous media pore size, and porous media heterogeneity. The asphaltene weight percent is also presented for all the experiments for both the produced oil and the bypassed oil, which is the unproduced oil that remained in the cell.

7.1. CO2 FLOW MECHANISM IN NANO-PORES

7.1.1. CO2 Injection Pressure Effect. Three CO_2 injection pressures were investigated in this research, including 200, 400, and 700 psi using 10 nm filter membrane. The results for the oil production with time, and the oil production rate with time are shown in Figure 4. Increasing the pressure from 200 to 400 psi resulted in an increase in the oil production and an increase in the oil production flow rate. Increasing the pressure to 700 psi resulted in a significant oil production increase, and also a very rapid oil production. The filter membrane for the 700 psi was analyzed for tears or degradation, and the experiment for the 700 psi was repeated five times to ensure that the result obtained was not affected by leakages or filter membrane degradation, and in each of the experiments, the same results were observed. The significant increase in oil recovery could be due to excessive oil swelling at that pressure, since oil swelling increases with increase in pressure, which may have reduced the oil viscosity, and increased its mobility significantly (Bahralolom, I. and Orr, F., 1988). The oil recovery percentages for all three experiments were calculated. The exact values are shown in Table 2. The 200 psi had an oil recovery of

13%, with an incremental 3.9% at 400 psi. Increasing the pressure to 700 psi however, resulted in an increment of 71.43%, which is considered a significantly large incremental oil recovery. These results can be correlated with the results in Figure 4 which shows the oil production and the oil production flow rate.

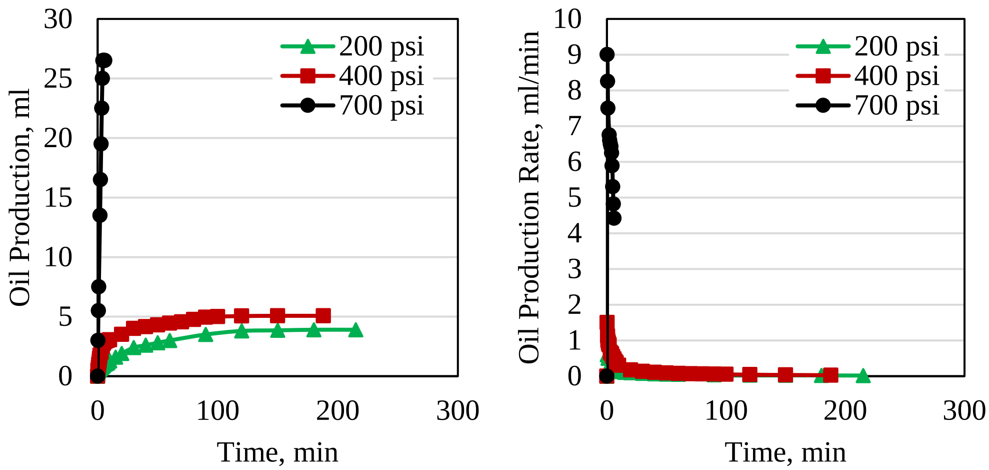

Figure 4. Oil Production and Oil Production Flow Rate at Different CO_2 Injection Pressure Using the 470 cp Oil and 100º C

Table 2. Oil Recovery for Different CO_2 Injection Pressures

CO_2 Injection Pressure, psi	Oil Recovery, %
200	13.00
400	16.90
700	88.33

7.1.2. Temperature Effect. The temperature of the experimental vessel was varied using the heating element in the support structure of the vessel. A 10 nm filter membrane was used to conduct the experiments. Three temperatures were investigated, including 60, 100, and 130 ºC. The results for the oil production and the oil production rate with time are shown in Figure 5. Increasing the temperature to 100 ºC resulted in an increase in oil recovery, and a decrease in gas breakthrough time. Increasing the temperature beyond 100 ºC resulted in a significant increase in recovery, and an extremely short gas breakthrough time. The 130 ºC experiment was also repeated five times with the same results being observed every time. The viscosity of the oil at 100 and 130 ºC were measured and were found to be 120.3 and 35.2 cp, respectively. This significant decrease in viscosity could be the main reason behind the increase in oil recovery and decrease in gas breakthrough time for the 130 ºC experiment. Table 3 shows the oil recovery percetages for all three temperatures used. The lowest temperature had a 7.17 % recovery, which is very small compared to the 91.67% obtained at the 130 ºC. There was a significant increment between the 100 and the 130 ºC.

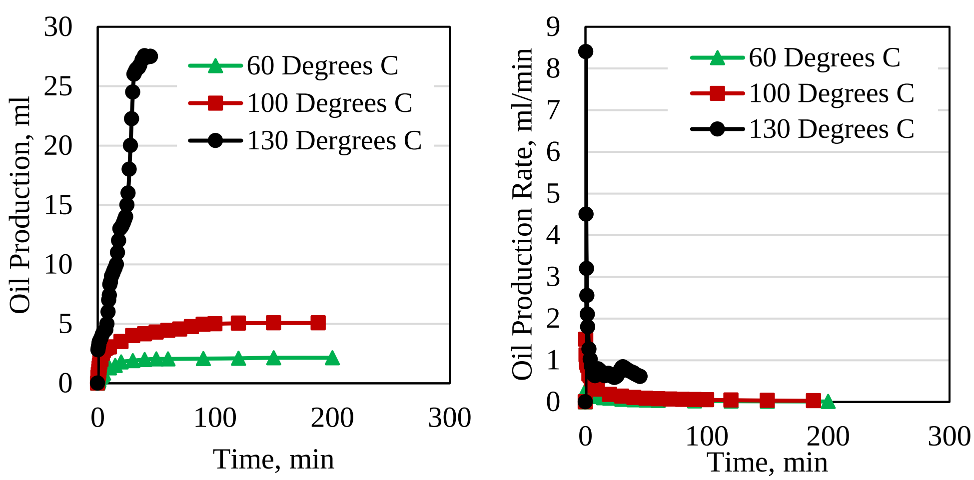

Figure 5. Oil Production and Oil Production Flow Rate at Different Temperatures Using the 470 cp Oil Viscosity and 400 psi CO_2 Injection Pressure

Table 3. Oil Recovery for Different Temperatures

Temperature, ºC	Oil Recovery, %
60	7.17
100	16.90
130	91.67

7.1.3. Oil Viscosity Effect. Three oil viscosity values including 470, 267, and 67 cp were investigated using 10 nm filter membrane. The results for the oil production and the oil production flow rate are shown in Figure 6. The results indicate that decreasing the oil viscosity will result in an increase in oil recovery. The lowest oil viscosity will therefore have the highest oil production flow rate as is shown in Figure 6. Table 4 summarizes all of the oil recovery percentages for different oil viscosity values. The lowest oil viscosity had a 58.33% recovery, compared to the 470 cp viscosity which resulted in a 16.83% recovery. Also, after measuring the aspahltene wt% for different oil viscosity values, it was found that the lowest oil viscosity had the lowest asphaltene wt%.

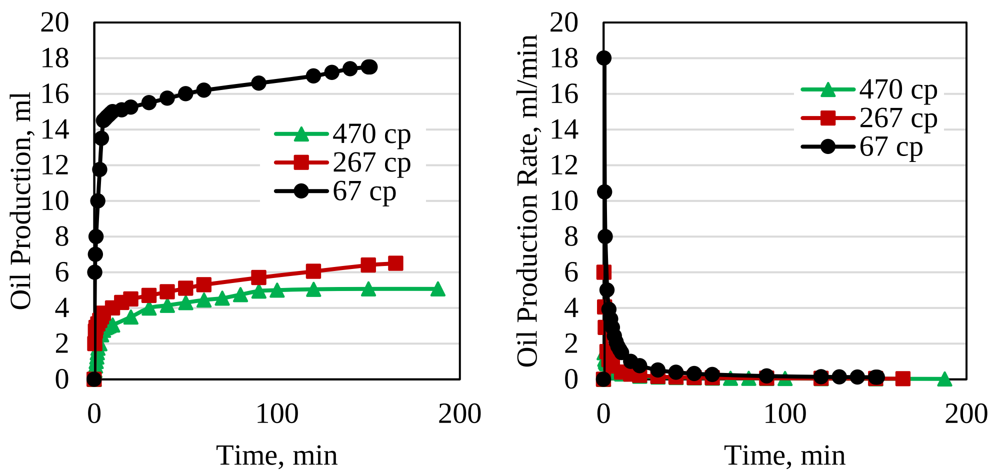

Figure 6. Oil Production and Oil Production Flow Rate Using Different Oil Viscosity Values at 400 psi CO_2 Injection Pressure and 100 ºC

Table 4. Oil Recovery Using Different Viscosity Oils

Oil Viscosity, cp	Oil Recovery, %
470	16.83
267	21.67
67	58.33

7.1.4. CO_2 Soaking Time Effect. The CO_2 soaking time is the time that the CO_2 is left in the reservoir to react with the oil prior to production. Two soaking times were investigated in this research, including 30 and 120 minutes, using 10 nm filter membrane. The lightest viscosity oil, 67 cp, was used in these two experiments. Figure 7 indicates that the longer the soaking time the higher the oil production and the higher the oil production flow rate as well. Table 5 summarizes the results for the oil recovery percentages using different CO_2 soaking times. The oil recovery for the 30 minutes soaking was less than half of that of the 120 minutes soaking, which shows that increasing the soaking time of the CO_2 will increase the oil recovery as well.

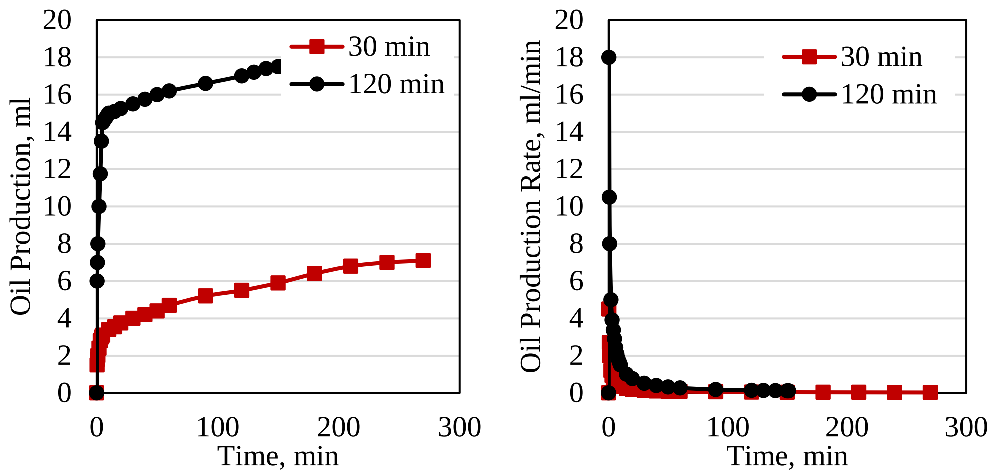

Figure 7. Oil Production and Oil Production Flow Rate for Different Soaking Times Using 67 cp Oil Viscosity at 400 psi CO_2 Injection Pressure and 100 °C

Table 5. Oil Recovery for Different CO_2 Soaking Times

CO_2 Soaking Time, min	Oil Recovery, %
30	23.67
120	58.33

7.1.5. Porous Media Thickness Effect. The thickness of the filter membranes was increased by stacking several filter membranes above each other. Each filter membrane had a thickness of 0.2 mm and 10 nm filter membrane. The membranes were all cut to the same size, and fixed to their place using a bottom cap bolted to the setup using six bolts to ensure that no leakage between the filter membranes occurred. Increasing the thickness of the filter membranes was studied in order to understand the behavior and oil recovery in a thicker porous media compared to the single filter membrane. Even though a core, or an actual reservoir will be much thicker than what was used in this study, the general effect can still be observed. Figure 8 illustrates that increasing the filter membrane thickness resulted in both a significant decrease in oil recovery, and an increase in CO_2 breakthrough time. Also, the oil production flow rate was decreased significantly as the thickness increased. This indicated that in a core plug or actual reservoir, the oil recovery could be severely lower that what was observed from the filter membranes. Table 6 summarizes the results of the oil recovery percentage using different filter membrane thicknesses. Since the porous media in the reservoir will be much larger than that conducted in the experiments, a larger decrease may be observed. One of the main contributors to the decrease in oil recovery is that the oil is absorbed by the thicker filter membranes between the layers due to the higher capillary pressure, and thus becomes trapped, which results in a decrease in oil recovery. Another main contributor to this decrease in oil recovery is the asphaltene precipitation.

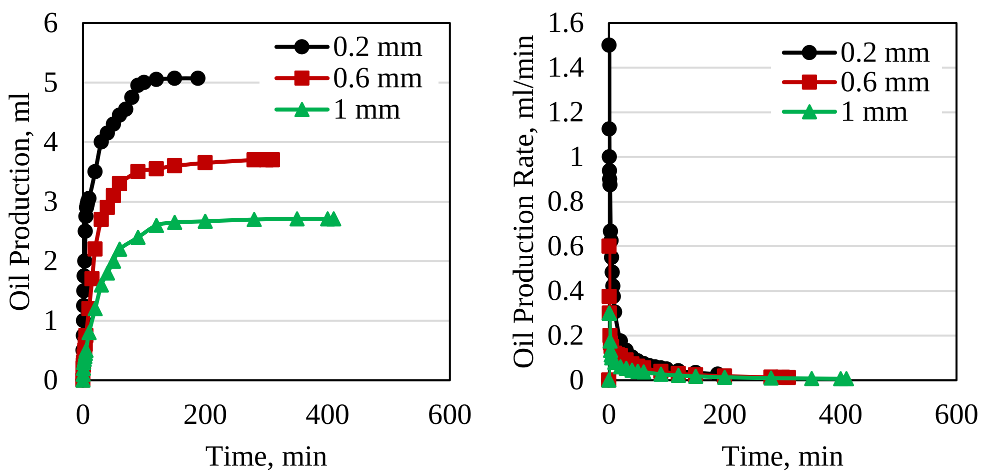

Figure 8. Oil Production and Oil Production Flow Rate Using Different Filter Paper Thicknesses at 400 psi CO_2 Injection Pressure and 100 °C using 470 cp Oil

Table 6. Oil Recovery for Different Filter Membrane Thicknesses

Filter Paper Thickness, mm	Oil Recovery, %
0.2	16.90
0.6	12.33
1	9.03

7.1.6. Porous Media Pore Size Effect. Three different nano-pore sizes were investigated in this research to cover the broadest range possible for the nano-pores. The pore size was varied using different filter membranes with pore sizes of 0.2, 10, and 100 nm. Figure 9 shows that no results are present for the 0.2 nm filter membrane. This is due to no oil production being observed from the 0.2 nm membrane even after 48 hours of continuous CO_2 injection and an increase in both temperature and pressure to 130 °C and

900 psi. This is mainly due to the capillary forces being extremely high and thus the pressure needed to overcome it would have been too high, and therefore no oil production occurred. Increasing the pore size from 10 nm to 100 nm however resulted in a significant increase in oil recovery, and a decrease in gas breakthrough time, where the gas breakthrough time using the 10 nm was after 188 minutes, and the gas breakthrough time was after 28 minutes only. This increase in oil recovery is due to the increased pore size which permitted the oil to be produced much easier due to the lower capillary forces. The oil production flow rate was also significantly high using the 100 nm filter membrane, and the oil recovery was the highest compared to all the other experiments using the 100 nm filter membrane. The oil recovery percentage for both experiments was summarized in Table 7.

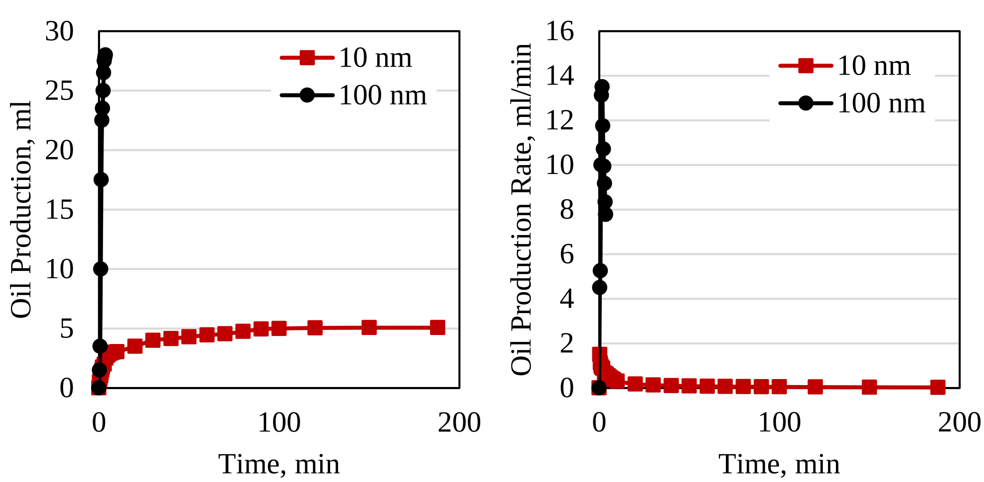

Figure 9. Oil Production and Oil Production Flow Rate Using Different Filter Paper Pore Size at 400 psi CO_2 Injection Pressure and 100 ºC using 470 cp Oil

Table 7. Oil Recovery for Different Filter Membrane Pore Sizes

Pore Size, nm	Oil Recovery, %
0.2	0.00
10	16.90
100	93.33

7.1.7. Porous Media Heterogeneity Effect. Heterogeneity is very common in the reservoir and is a major cause of many production problems. This research investigates the effect of heterogeneity on CO_2 flow behavior and oil recovery. Heterogeneity was created by combining three filter membranes together with the top and bottom filter membranes of pore size 100 nm and the middle filter membrane of pore size 10 nm. The results obtained from the heterogeneity experiment were compared to the single 10 nm experiment and the triple 10 nm filter membrane experiment. Figure 10 shows the oil recovery from the heterogeneity experiment was slightly less than that of the single 10 nm experiment due to the presence of the two 100 nm filter membranes which created a slight hindrance to the oil flow due to the small increase in capillary pressure and the adsorption of the oil on the filter membranes. The heterogeneity experiment showed more oil recovery than that of the three 10 nm experiment however, since the 100 nm filter membranes will have a much smaller impact on oil recovery compared to the 10 nm membranes since the oil will flow much more easily through the larger pores. The oil recovery percentages were calculated for the heterogeneity experiment and compared to both the single and triple 10 nm filter membranes experiments as well; the values are presented in Table 8. All filter membranes had the same diameter in order to be able to stack them together uniformly, and to ensure that no leakages occur.

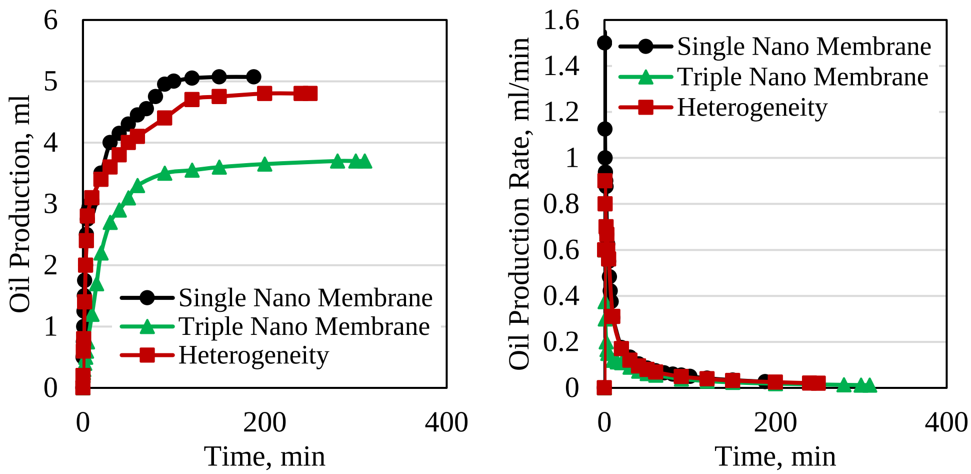

Figure 10. Effect of Heterogeneity on Oil Production and Oil Production Flow Rate at 400 psi CO_2 Injection Pressure and 100 ºC using 470 cp Oil

Table 8. Oil Recovery for Heterogeneity Run Compared to Homogenous Runs

Pore Size, nm	Oil Recovery, %
Single	16.90
Triple	12.33
Heterogeneity	16.00

7.2. ASPHALTENE PRECIPITATION AND DEPOSITION

The asphaltene weight percent was measured for all the experiments explained above. Initially, the asphaltene weight percent of the original crude oil was measured before running CO_2 injection experiments. The asphaltene weight percent for all the oil viscosity values used are shown in Table 9.

Decreasing the oil viscosity results in a decrease in the asphaltene weight percent. This is one of the main reasons why a lower oil production was obtained for the higher viscosity oil as shown previously, and will also be important when explaining the asphaltene weight percent in the produced and bypassed oil at different oil viscosity values as well The asphaltene content varies with the changes in oil viscosity; which will be explained later on when explaining the oil viscosity.

Table 9. Asphaltene Weight Percent for the Pure Crude Oil

Oil Viscosity, cp	Asphaltene Weight Percent, %
470	5.73
267	4.63
67	3.22

7.2.1. CO_2 Injection Pressure Effect. The asphaltene weight percent for both the produced and bypassed oil at different CO_2 injection pressures are shown in Table 10. As the pressure increases, the asphaltene weight percent for the produced oil also increases due to the oil being forced through the filter membrane. The bypassed oil asphaltene weight percent decreased with the increase in pressure due to more asphaltene being produced with the oil. This asphaltene was forced through the filter membranes, which indicates that in real cores the behavior could be different since they will have a much larger thickness.

Table 10. Asphaltene Wt% for Produced and Bypassed Oil at Different CO_2 Pressures

CO_2 Injection Pressure, psi	Produced Oil Asphaltene Wt %	Bypassed Oil Asphaltene Wt%
200	1	28
400	1.4	18
700	1.4	14

7.2.2. Temperature Effect. Increasing the temperature will result in an instability in the equilibrium of the oil, which in turn will increase asphaltene precipitation and pore plugging. The asphaltene weight percent for the produced and the bypassed oil at different temperatures are shown in Table 11. Increasing the temperature resulted in an increase in asphaltene weight percent in the bypassed oil which indicated a high percentage of asphaltene precipitation in the porous media. The produced oil asphaltene weight percent decreased with the increase in temperature since much of the asphaltene had precipitated during the soaking period and so the oil produced had a much smaller asphaltene weight percent.

Table 11. Asphaltene Wt% for Produced and Bypassed Oil at Different Temperatures

Temperature, ºC	Produced Oil Asphaltene Wt %	Bypassed Oil Asphaltene Wt%
60	1.4	16
100	1.2	18
130	1	20

7.2.3. Oil Viscosity Effect. As was stated earlier in Table 9, the lower viscosity oil had a smaller asphaltene weight percent compared to the higher viscosity oil. Table 12 shows the results for the produced and bypassed oil asphaltene weight percent for different viscosity oils. The results show a similar trend compared to those in Table 9 where the lower viscosity oil still had a much lower asphaltene weight percent for both the produced and the bypassed oil compared to the higher viscosity oils.

Table 12. Asphaltene Wt% for Produced and Bypassed Oil Using Different Viscosity

Oil Viscosity, cp	Produced Oil Asphaltene Wt%	Bypassed Oil Asphaltene Wt%
470	1.4	18
267	1.2	14
67	0.8	10

7.2.4. CO_2 Soaking Time Effect. Increasing the CO_2 soaking time increases the duration of the interaction of the CO_2 with the oil thus, this increased interaction will result in a higher percentage of asphaltene precipitation. Results summarized in Table 13 show that asphaltene weight percent in the bypassed oil, is higher for the 120 minutes soaking time compared to the 30 minutes soaking time.

Table 13. Asphaltene Wt% for Produced and Bypassed Oil at Different Soaking Times

CO_2 Soaking Time, min	Produced Oil Asphaltene wt%	Bypassed Oil Asphaltene wt%
30	2	8
120	0.8	10

7.2.5. Porous Media Thickness Effect. As explained before, increasing the filter membrane thickness will result in some of the oil being adsorbed on the filter membrane, and trapped between the layers. The oil will travel through the filter membranes, and during that time, asphaltene precipitation will take place. This resulted in a larger percentage of asphaltene precipitation, as shown in Table 14. The 1 mm filter paper thickness had an asphaltene weight percent in the bypassed oil of 44%, which is the highest value obtained in this study. Since the oil produced had to extrude through a thicker membrane, it had an extremely low asphaltene weight percent compared to the bypassed oil. Increasing the filter membrane thickness may result in an even more severe asphaltene precipitation.

Table 14. Asphaltene Wt% for Produced and Bypassed Oil for Different Thickness

Filter Paper, mm	Produced Oil Asphaltene Wt %	Bypassed Oil Asphaltene Wt%
0.2	1.4	18
0.6	1.2	30
1	0.8	44

7.2.6. Porous Media Pore Size Effect. The asphaltene weight percent for the produced and bypassed oil using different pore sizes is shown in Table 15. The 0.2 nm filter membrane has no results since no oil was produced from that membrane. The 100 nm membrane showed interesting results; the asphaltene weight percent in the produced oil was 4.33%, which is very close to the 5.73% found in the pure crude oil in Table 9. This shows that the severity of asphaltene precipitation and pore plugging decreased significantly with the increase in pore size since both oils had a very close asphaltene weight percent. These results imply that asphaltene precipitation in unconventional reservoirs could be much more severe compared to precipitation in conventional oil reservoirs due to the extreme difference in pore size. The asphaltene weight percent in the bypassed oil was the lowest value found for all the experiments conducted using the 470 cp oil at the conditions at which the experiments were conducted.

Table 15. Asphaltene Wt% for Produced and Bypassed Oil for Different Pore Sizes

Pore Size, nm	Produced Oil Asphaltene Wt %	Bypassed Oil Asphaltene Wt%
0.2	-	-
10	1.4	18
100	4.33	16

7.2.7. Porous Media Heterogeneity Effect. The asphaltene weight percent from the heterogeneity experiment is summarized in Table 16, and is compared to the single and triple 10 nm experiment. Both the value of asphaltene weight percent for the produced and bypassed oil lie between the single and triple 10 nm experiments. This is due to the two 100 nm filter membranes resulting in a slightly higher asphaltene weight percent in the bypassed oil compared to the single 10 nm experiment, and a lower asphaltene weight percent compared to the triple 10 nm experiment. Heterogeneity using smaller pore size filter membranes could have resulted in a different conclusion, and thus further investigation regarding heterogeneity is needed in order to fully understand the effect of this phenomenon on asphaltene pore plugging and oil recovery. Also, heterogeneity will be much more severe in cores and real field compared to the filter membranes.

Table 16. Asphaltene Wt% for Produced and Bypassed Oil For Heterogeneity Run

Pore Size, nm	Produced Oil Asphaltene Wt %	Bypassed Oil Asphaltene Wt%
Single	1.4	18
Triple	1.2	30
Heterogeneity	1.3	22

8. DISCUSSION

Two of the main factors studied in this research are the CO_2 operating conditions, which include CO_2 injection pressure and CO_2 soaking time, and the nano-pore size of unconventional shale reservoirs, which includes the filter membrane pore size, the filter membrane thickness, and the pore size heterogeneity. These factors showed a significant impact on both oil recovery, and asphaltene precipitation and deposition. Table 17 below shows the oil recovery percentage and the asphaltene weight percent for both the produced oil and the bypassed oil for all the factors that are directly related to the CO_2 operating conditions and shale nano-pore size. Also, the asphaltene weight percentage increase from the original asphaltene weight percentage is shown in Table 17. This increase in asphaltene weight percent was calculated by subtracting the asphaltene weight percent in the original oil from the asphaltene weight percent in the bypassed oil. This value is a direct indication of asphaltene pore plugging potential since it shows the extent to which asphaltene percentage will increase in the unproduced oil, and thus the extent to which asphaltene pore plugging may occur. For the 200 psi CO_2 injection pressure, the asphaltene weight percent increased from 5.73% to 28% in the bypassed oil, which represents a 22.27% increase from the original value. The summary provided in the table can help illustrate the impact of different factors on asphaltene, and compare these factors together in order to understand which factor may have a more significant impact; this will be illustrated furthermore in the pareto plot generated in this research.

Table 17. Effect of CO_2 Conditions and Pore Size on Oil Recovery and Asphaltene %

Factor Wt%	No.	Oil Recovery %	Pure Oil Asphaltene	Produced Oil	Bypassed Oil	Asphaltene wt% Increase
CO_2 Injection Pressure, psi	200	13.00	5.73	1	28	22.27
	400	16.90	5.73	1.4	18	12.27
	700	88.33	5.73	1.4	14	8.27
CO_2 Soaking Time, min	30	23.67	3.22	2	8	4.78
	120	58.33	3.22	0.8	10	6.78
Membrane Pore Size, nm	0.2	-	5.73	-	-	-
	10	16.90	5.73	1.4	18	12.27
	100	93.33	5.73	4.33	16	10.27
Membrane Thickness, mm	0.2	16.90	5.73	1.4	18	12.27
	0.6	12.33	5.73	1.2	30	24.27
	1	9.03	5.73	0.8	44	38.27
Heterogeneity	-	16.00	5.73	1.3	22	16.27

In order to evaluate the impact of each of the factors studied in this research on asphaltene precipitation, a Pareto plot was generated. The Pareto plot can be used to evaluate the percentage effect of different factors on an objective function, which is the asphaltene precipitation in this case. The Pareto plot is shown in Figure 11. The filter membrane thickness had the strongest impact on asphaltene precipitation. This indicates that in cores or actual reservoirs, as opposed to the filter membranes used in this study, the asphaltene precipitation will be much more severe. The pressure also had a significant effect on asphaltene precipitation, with a 21.21% impact. The remaining factors also had an impact on asphaltene precipitation, however their impact was smaller than the others. This Pareto plot was generated based on the results obtained from this research alone, and thus cannot be generalized on all cases involving asphaltene. Also, the plot is based on a limited number of factors, that were investigated in this research.

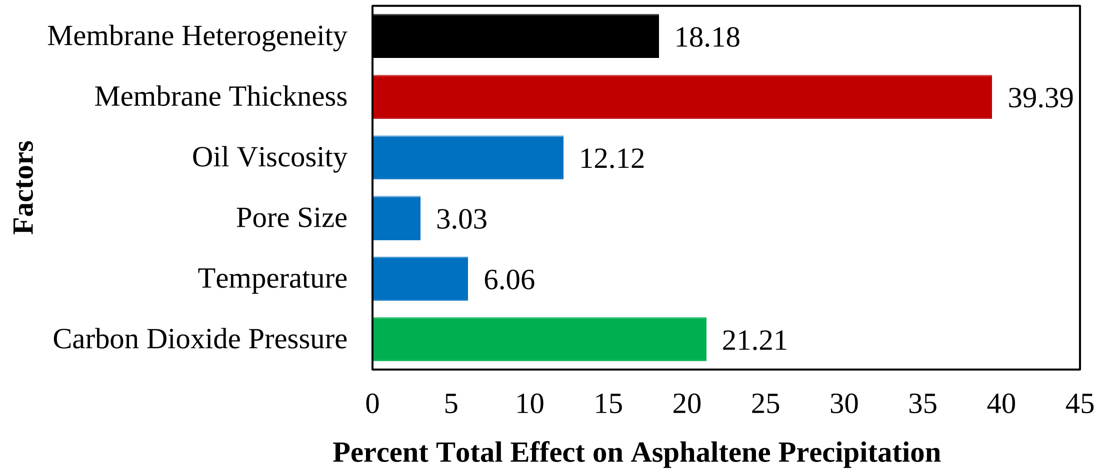

Figure 11. Pareto Plot Showing Effect of Different Factors on Asphaltene Precipitation

9. CONCLUSIONS

This research conducted experiments using nano composite filter membranes to investigate the CO_2 flow mechanism in unconventional nano-pores of oil reservoirs by varying CO_2 injection pressure, temperature, oil viscosity, CO_2 soaking time, porous media thickness and heterogeneity. The research also investigated asphaltene precipitation and deposition in the nano-pores and the severity of this precipitation by quantifying the asphaltene wt% from all experiments conducted. The main conclusions reached from this research are shown below.

- As the CO_2 injection pressure increased, the oil production increased, and the gas breakthrough time decreased. The asphaltene weight percent for the produced oil also increased with the increase in CO_2 injection pressure due to the CO_2 forcing the oil through the pores.

- Increasing the temperature also resulted in an increase in oil recovery, and also a decrease in CO_2 breakthrough time due to the decrease in oil viscosity. Increasing the temperature resulted in a higher asphaltene weight percent for the bypassed oil however, due to the instability of the resin at high temperature.
- Increasing the oil viscosity resulted in a decrease in oil production, and a prolonged gas breakthrough time. The asphaltene weight percent increased with the increase in oil viscosity for both the produced oil and the bypassed oil.
- Heterogeneity and increase in filter paper thickness also resulted in a decrease in oil recovery. The asphaltene weight percent in the bypassed oil also increased for both, which is an indication that the asphaltene pore plugging could be a serious issue in real reservoirs.
- Increasing CO_2 soaking time resulted in a higher asphaltene weight percent in the bypassed oil since the oil becomes more unstable, however, it yielded a higher oil recovery due to the prolonged interaction of the CO_2 with the oil, and also the prolonged oil subjection to temperature.
- Pore size increase resulted in a reduced asphaltene weight percent and also a higher oil recovery. This is a strong indication to the severity of asphaltene pore plugging in the smaller nano-pores of unconventional oil reservoirs compared to conventional oil reservoirs.
- Using the Pareto Plot, it was found that the filter membrane thickness had the strongest impact on asphaltene precipitation, followed by the CO_2 injection pressure, and the pore size heterogeneity.

NOMENCLATURE

nm	Nanometer
wt%	Weight Percent
wt_{asph}	Asphaltene Weight Percent
wt_{oil}	Oil Weight Percent
cp	Centipoise
C	Celsius
mm	Millimeter
Psi	Pound per Square Inch

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SECTION

3. CONCLUSIONS AND RECOMMENDATIONS

3.1. CONCLUSIONS

A comprehensive data analysis on asphaltene properties, characteristics, and factors impacting asphaltene stability in the crude oil. After performing the data analysis, experiments were conducted to study and quantify the effect of the factors that were found to have an effect on asphaltene stability in the comprehensive data analysis. The findings from this research are summarized as follows:

- Asphaltene concentration in crude oils varies significantly and can reach as high as 43 wt% in some cases such as bitumen.
- Even the highest API gravity oils can still contain a percentage of asphaltene in their composition, which indicates that asphaltenes can be found in different classifications of crude oil and is not only confined to low API gravity oils as is commonly believed.
- Asphaltene liberation from crude oil can form at multiple temperatures and pressures depending on the properties of the crude oil and its composition.
- The highest frequency range of permeability was between 0-10 mD, which indicates that asphaltene pore plugging will be significant in the low permeability formations compared to the higher permeability ones.
- Asphaltene pore plugging experiments have focused mainly on sandstone and carbonate reservoirs, with very little work conducted on shale.

- Most of the asphaltene field cases reported worldwide were in the Middle East and the United States of America.
- The thermodynamic conditions, including pressure and temperature, had a strong impact on asphaltene liberation. These two factors are very difficult to control since they are intrinsic properties of the reservoir.
- The lighter oil with a lower viscosity was found to have a lower asphaltene concentration, which follows the Yen-Mullins Asphaltene Model, which classifies asphaltene based on its size according to the oil type.
- The lower the filter membrane size, the larger the asphaltene concentration in the filtride, bypassed oil. This is an indication that asphaltene pore plugging will be significantly higher in unconventional reservoirs with nanopores compared to conventional reservoirs. The same result can be supported using the comprehensive data analysis conducted.
- Increasing the filter membrane thickness and heterogeneity resulted in a larger asphaltene content in the bypassed oil. This indicates that asphaltene pore plugging may be extremely severe in cores and actual reservoirs compared to the extremely thin filter membranes.

3.2. RECOMMENDATIONS

This research investigated asphaltene in crude oil by undergoing a comprehensive data analysis to determine the factors that have a strong impact on asphaltene equilibrium in crude oil and study the most common frequency ranges for these factors. The research also underwent experiments to investigate the impact of these factors on asphaltene concentration and oil recovery. There are much more topics that can be investigated pertaining to asphaltenes in order to obtain a comprehensive understanding of its properties and impact on crude oil. These include:

- Investigate asphaltene precipitation, flocculation, and deposition using Multi-Filter Membrane model, which incorporates more than one filter membrane.
- Study the extent to which asphaltene precipitation will occur in shale cores during solvent injection using imaging techniques such as Seismic Electron Microscope (SEM) and Computer Tomography Scanning (CT).
- Determine the impact of CO_2 miscibility on asphaltene stability in crude oil during CO_2 injection and flooding.
- Study the use of different solvents, other than CO_2, such as nitrogen, on asphaltene stability in the crude oil.
- Match and upscale the experimental results using reservoir simulation software to study asphaltene precipitation and its impact on oil recovery on the reservoir scale.
- Study the impact of electro-kinetic effect, which involves charges and velocity, on asphaltene precipitation and deposition.
- Develop a mathematical equation to be able to model asphaltene precipitation during solvent injection (flooding and cyclic).

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VITA

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